QUANTA CHEMISTRY

An Institute of Chemical Sciences

CHEMICAL KINETICS

DPP-1

1. If the rate laws are expressed in concentration unit mol dm^{-3}, the unit of the third order reaction rate constant is

   (a) $dm^3\ mol^1\ sec^1$ (b) $dm^3\ mol^{-1}\ sec^{-1}$

   (c) $dm^6\ mol^{-2}\ sec^{-1}$ (d) $dm^{-3}\ mol1\ sec^{-1}$

2. The differential rate law equation for the elementary reaction

   $A + 2B \xrightarrow{k} 3C,$ is

   (a) $-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A][B]^2$

   (b) $-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = k[A]^2[B]$

   (c) $-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = k[A][B]^2$

   (d) None of these

3. For the reaction: 2A → B + 3C; if $-\frac{d[A]}{dt} = k_1[A]^2 \frac{d[B]}{dt} = k_2[A]^2; \frac{d[C]}{dt} = k_3[A]^2$ the correct relation between k_1 , k_2 and k_3 is :

   (a) $k_1 = k_2 = k_3$

   (b) $2k_1 = k_2 = 3k_3$

   (c) $4k_1 = k_2 = 3k_3$

   (d) $\frac{k_1}{2} = k_2 = \frac{k_3}{3}$

4. For a reaction, 2A + B → 3Z, if the rate of consumption of A is 2×10^{-4} mol dm^{-3} s^{-1} the rate of formation of Z (in mol dm^{-3} s^{-1}) will be

   (a) 3×10^{-4} (b) 2×10^{-4}

   (c) $\frac{4}{3} \times 10^{-4}$ (d) 4×10^{-4}

5. If the unit of the rate constant of a reaction is $L^3\ mol^{-3}s^{-1}$, the order of the reaction is

   (a) 1 (b) 2

   (c) 3 (d) 4

6. Consider the chemical reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$. The rate of this reaction can be expressed in term of time derivative of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expressions.

   (a) Rate = $-\, d[N_2]/dt = -\, 1/3\, d[H_2]/dt = 1/2 d[NH_3]/dt$

   (b) Rate = $-\, d[N_2]/dt = -\, 3d[H_2]/dt = 2d[NH_3]/dt$

   (c) Rate = $d[N_2]/dt = 1/3\, d[H_2]/dt = 1/2 d[NH_3]/dt$

   (d) Rate = $-\, d[N_2]/dt = -\, d[H_2]/dt = d[NH_3]/dt$

7. The rate of a reaction is expressed in different ways as follows :

$$+\frac{1}{2}\frac{d[C]}{dt} = \frac{1}{3}\frac{d[D]}{dt} = +\frac{1}{4}\frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

   The reaction is:

   (a) $4\,A + B \longrightarrow 2C + 3D$ (b) $B + 3\,D \longrightarrow 4\,A + 2\,C$

   (c) $A + B \longrightarrow C + D$ (d) $B + D \longrightarrow A + C$

8. The rate constant for the reaction

   $2N_2O_5 \longrightarrow 4NO_2 + O_2$

   is 3.0×10^{-5} sec^{-1}. If the rate is 2.4×10^{-5} mol litre^{-1} sec^{-1}, then the concentration of N_2O_5 (in mol litre^{-1}) is

   (a) 1.4 (b) 1.2

   (c) 0.004 (d) 0.8

9. Ammonia and oxygen reacts at higher temperatures as

   $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

   In an experiment, the concentration of NO increases by 1.08×10^{-2} mol litre^{-1} in 3 seconds. Calculate.

   (i) rate of reaction.

   (ii) rate of disappearance of ammonia

   (iii) rate of formation of water

10. Dinitropentaoxide decomposes as follows :

$$N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$

   Given that $-d[N_2O_5]/dt = k_1[N_2O_5]$

   $d[NO_2]/dt = k_2[N_2O_5]$

   $d[O_2]/dt = k_3[N_2O_5]$

   What is the relation between k_1, k_2 and k_3?

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ANSWERS

1.(c) 2.(c) 3.(d) 4.(a) 5.(d) 6.(a) 7.(b) 8.(d)

9. (i) 9×10^{-4} mol litre^{-1} sec^{-1}, (ii) 36×10^{-4}mol litre^{-1}sec^{-1}, (iii) 54×10^{-4} mol litre^{-1} sec^{-1}

10.(b)

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CHEMICAL KINETICS

DPP-2

1. For the reaction $2NO_{(g)} + 2H_{2(g)} \rightarrow N_2(g) + 2H_2O_{(g)}$ the rate expression can be written in the following ways

$\frac{d[N_2]}{dt} = k[NO][H_2]$ $\quad$ $\frac{d[H_2O]}{dt} = k_1[NO][H_2]$

$\frac{d[NO]}{dt} = k'_1[NO][H_2];$ $\quad$ $\frac{d[H_2]}{dt} = k''_1[NO][H_2]$

The relationship between k, k_1, k'_1 and k''_1 is :

(a) $k = k_1 = k'_1 = k_1^-$ $\quad$ (b) $k = 2k_1 = k'_1 = k_1^-$

(c) $k = 2k'_1 = k_1 = k_1^-$ $\quad$ (d) $k'_1 = k''_2 = 2k_1 = k$

2. Which of the following statement is incorrect?

(a) Unit of rate of disappearance is Ms^{-1} $\quad$ (b) Unit of rate of reaction is Ms^{-1}

(c) Unit of rate constant k is depend on order $\quad$ (d) Unit of k for first order reaction is Ms^{-1}

3. In the following reaction, how is the rate of appearance of the underlined product related to the rate of disappearance of the underlined reactant, $\underline{BrO_3^-}(aq) + 5Br^-(aq) + 6H^-(aq) \rightarrow 3\underline{Br_2}(l) + 3H_2O(aq)$

(a) $-\frac{d[BrO_3^-]}{dt} = \frac{d[Br_2]}{dt}$ $\quad$ (b) $-\frac{1}{3}\frac{d[BrO_3^-]}{dt} = \frac{d[Br_2]}{dt}$

(c) $\frac{-d[BrO_3^-]}{dt} = \frac{1}{3}\frac{d[Br_2]}{dt}$ $\quad$ (d) None of these

4. If $r = k[A]_0^2[B]_0$ for a reaction, by what factor is the initial rate multiplied if the $[A]_0$ is multiplied by 1.5 and the $[B]_0$ is tripled?

(a) 4.5 $\quad$ (b) 2.25

(c) 6.75 $\quad$ (d) None of these

5. The unit of rate constant of zero order and first order chemical reactions are respectively.

(a) $molL^{-1}s^{-1}, molL^{-1}s^{-1}$ $\quad$ (b) $s^{-1}, molL^{-1}s^{-1}$

(c) $molL^{-1}s^{-1}, s^{-1}$ $\quad$ (d) None of these

6. How will the rate of the reaction $\left(rate = k[NO]^2[O_2]\right)$ change if the volume of the reaction vessel is reduced to one third?

(a) It will diminish to 1/27 to the initial value

(b) It will diminish to 1/9 of the initial value.

(c) It will increase by 27 times.

(d) It will increase by 9 times.

7. Reaction A +B $\rightarrow$ C + D follows rate law, r = k $[A]^{1/2}$ $[B]^{1/2}$ starting with 1M of A and B each. What is the time taken for concentration of a becomes 0.1 M?

(a) 10 sec (b) 100 sec

(c) 1000 sec (d) 434 sec

8. For the reaction $2X_3 = 3X_2$, the rate of formation of X_2 is :

(a) $3\left(-d[X_3]/dt\right)$ (b) $\frac{1}{2}\left(-d[X_3]/dt\right)$

(c) $\frac{1}{3}\left(-d[X_3]/dt\right)$ (d) $\frac{3}{2}\left(-d[X_3]/dt\right)$

9. For the reaction : $Br_2(g) + BF_2(g) \rightarrow 2BrF_3(g)$, the equilibrium constant at 2000 K and 1.0 bar is 5.25. When the pressure is increased by 8-fold, the equilibrium constant.

(a) Increase by a factor of 1.86 (b) Decrease by a factor of 1.86

(c) Remains same (d) Increases by a factor of 8

10. The reaction A (g) + 2B (g) $\rightarrow$ C(g) is an elementary reaction. In an experiment involving this reaction, the initial partial pressure of A and B are P_A = 0.40 atm and P_B = 1.0 atm respectively. When P_e = 0.3 atm, the rate of the reaction relative to the initial rate is :

(a) 1/12 (b) 1/50

(c) 1/25 (d) None of these

11. Which of the following statement is incorrect about order of reaction?

(a) Order of reaction is determined experimentally

(b) It is the sum of power of concentration terms in the rate law expression

(c) It does not necessarily depend on stoichiometric coefficients

(d) Order of the reaction can not have fractional value

12. For any reaction,

A + B $\rightarrow$ C + D

Rate law obtained is : Rate = k[A] [B]

Select the correct option

(a) Reaction must be elementary (b) Reaction must be complex

(c) Reaction may be elementary or complex (d) None of these

13. A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will

(a) Double (b) remain unchanged

(c) Triple (d) Increase by a factor of 4

14. The rate law for a reaction between the substances A and B is given by

rate = k $[A]^n$ $[B]^m$

On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as

(a) 2 (n–m) (b) 1 / 2 (m+n)

(c) (m + n) (d) (n – m)

15. Which of the following is/are correct statement?

(a) Stoichiometry of a reaction tells about the order of the elementary reactions.

(b) For a zero order reaction, rate and the rate constant are identical.

(c) A zero order reaction is controlled by factors other than concentration of reactants.

(d) A zero order reaction is always elementary reaction.

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ANSWERS

1.(d) 2.(d) 3.(c) 4.(c) 5.(c) 6.(c) 7.( ) 8.(d) 9. (c) 10.(c) 11.(d) 12.(c) 13.(d) 14.(b) 15. (a,b,c)

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CHEMICAL KINETICS

DPP-3

1. For a second order reaction A + B $\rightarrow$ products, where the initial concentration of the reactants are the same (x mol/lit) and k is the rate constant, the half- life of the reaction is :

   (a) 1/kx (b) 0.693/k

   (c) 0.5/k (d) 0.5 kx

2. For a first order reaction, the half-life is 50s. Identify the correct statement form the following.

   (a) The reaction is complete in 100s

   (b) The reaction begins after 50s

   (c) The same quantity of A is consumed for every 50s of the reaction.

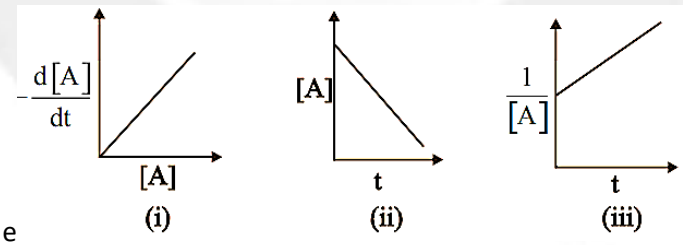
   (d) Quantity of A remaining after 100s is half of what remains after 50s.

3. If the concentration vs time plot is found to be linear with a negative slope, the order of the reaction is:

   (a) 0 (b) 1

   (c) 2 (d) Can not be determined.

4. Consider the plots for the types of reaction, nA $\rightarrow$ B + C. These plots respectively correspond to the reaction orders :



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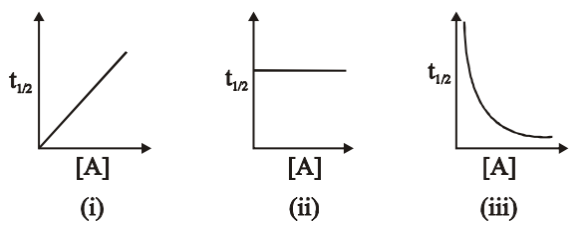
   (a) 0, 2, 1 (b) 0, 1, 2

   (c) 1, 1, 2 (d) 1, 0, 2

5. Consider the plots, given below, for the types of reaction: nA $\rightarrow$ B + C. These plots respectively correspond to the reaction orders :



   (a) 0, 1, 2 (b) 1, 2, 0

   (c) 1, 0, 2 (d) None of these

6. $A_2 + B_2 \rightarrow 2AB$; R.O.R. = k $[A_2]^a$ $[B_2]^b$

Initial $[A_2]$	Initial $[B_2]$	R.O.R. (r)
0.2	0.2	0.04
0.1	0.4	0.04
0.2	0.4	0.08

Order of reaction with respect to A_2 and B_2 are respectively :

(a) a = 1, b = 1 (b) a = 2, b = 0

(c) a = 2, b = 1 (d) None

7. What type of reaction is this ?

$$CH_3COOC_2H_5(aq) + H_2O(l) \xrightarrow{H^+(aq)} CH_3COOH(aq) + C_2H_5OH(aq)$$

(a) Unimolecular elementary (b) Pseudo first order

(c) Zero order (d) Second order

8. When ethyl acetate was hydrolyzed in presence of 0.1 N HCl, the rate constant was found to be $6.25 \times 10^{-5} s^{-1}$. But in presence of 0.1 N H_2SO_4 the rate constant was found to be $5.4 \times 10^{-5} s^{-1}$. Thus it may be concluded that :

(a) H_2SO_4 is furnish more H^+ than HCl (b) H_2SO_4 is furnished lesser H^+ than HCl

(c) Both have the same strength (d) Will depend on concentration of ethyl acetate.

9. In the following reaction A $\rightarrow$ B + C, rate constant is 0.001 Ms^{-1}. If we start with 1 M of A then conc. of A and B after 10 minutes are respectively :

(a) 0.5 M, 0.5 M (b) 0.6 M, 0.4 M

(c) 0.4 M, 0.6 M (d) None of these

10. Half-life ($t_{1/2}$) and completion time (T) of the given reaction are :

3A $\xrightarrow{K}$ rate law k [$k = 1 \times 10^{-3}$ Ms^{-1}, a = 1M]

(a) 500 min, 750 min (b) 500 sec, 750 sec

(c) 500 sec, 1000 sec (d) None of these

11. For the zero order reaction A $\rightarrow$ B + C; initial concentration of A is 0.1 M. If A = 0.08 M after 10 minutes, then its half-life and the completion time are respectively

(a) 10 min; 20 min (b) 2×10^{-3} min; 4×10^{-3} min

(c) 25 min; 50 min (d) 250 min, 500 min

12. The decomposition of azo methane, at certain temperature according to the equation

$(CH_3)_2N_2 \rightarrow C_2H_6 + N_2$ is a first order reaction.

After 40 minutes from the start, the total pressure developed is found to be 350 mm Hg in place of initial pressure 200 mm Hg of azo methane. The volume of rate constant k is :

(a) 2.88×10^{-4} sec^{-1} (b) 1.25×10^{-4} sec^{-1}

(c) 5.77×10^{-4} sec^{-1} (d) None of these

13. For a particular reaction with initial conc. of the reactants as a_1 and a_2, the half-life period are t_1 and t_2 respectively. The order of the reaction (n) is given by :

(a) $n = 1 + \frac{\log(t_2/t_1)}{\log(a_2/a_1)}$ (b) $n = 1 + \frac{\log(a_2/a_1)}{\log(t_2/t_1)}$

(c) $n = 1 + \frac{\log(t_2/t_1)}{\log(a_2/a_1)}$ (d) None of these

14. At 300K the half-life of a sample of a gaseous compound initially 1 atm is 100 sec. When the pressure is 0.5 atm the half-life is 50 sec. The order of reaction is :

(a) 0 (b) 1

(c) 2 (d) 3

15. The kinetic data for the given reaction $A(g)+2B(g) \xrightarrow{k} C(g)$ is provided in the following table for three experiments at 300 K.

Ex. No.	[A / M]	[B / M]	Initial rate (M sec^{-1})
1	0.01	0.01	6.930×10^{-6}
2	0.02	0.01	1.386×10^{-5}
3	0.02	0.02	1.386×10^{-5}

In another experiment starting with initial concentration of 0.5 and 1 M respectively for A and B at 300 K, find the rate of reaction after 50 minutes from start of experiment (in M/sec).

(a) 6.93×10^{-4} (b) 0.25×10^{-7}

(c) 4.33×10^{-5} (d) 3.46×10^{-4}

16. The reaction A(g) + 2B(g) $\rightarrow$ C(g) is an elementary reaction. In an experiment involving this reaction, the initial partial pressure of A and B are P_A = 0.40 atm and P_B = 1.0 atm respectively. When P_0 = 0.3 atm, the rate of the reaction relative to the initial rate is :

(a) 1/12 (b) 1/50

(c) 1/25 (d) None of these

17. The reaction A(g) + 2B(g) $\rightarrow$ C(g) is a first order reaction with rate constant 2.772×10^{-3} s^{-1} . Starting with 0.1 mole of A in 2 litre vessel, find the concentration of A after 250 sec. When the reaction is allowed to take place at constant pressure at 300 K.

(a) 0.0125 M (b) 0.025 M

(c) 0.05 M (d) none of these

18. For a first order homogenous gaseous reaction A $\rightarrow$ 2B + C If the total pressure after time t was P_t and after long time ($t \rightarrow \infty$) was P_∞ then k in terms of P_t , P_∞ and t is:

(a) $k=\frac{2.303}{t}\log\left(\frac{P_\infty}{P_\infty-P_t}\right)$ (b) $k=\frac{2.303}{t}\log\left(\frac{2P_\infty}{P_\infty-P_t}\right)$

(c) $k=\frac{2.303}{t}\log\left(\frac{2P_\infty}{3(P_\infty-P_t)}\right)$ (d) None of these

19. A(aq) $\rightarrow$ B(aq) + C(aq) is a first order reaction.

Time t

mole of reagent n_1 n_2

Reaction progress is measure with the help of titration of reagent 'R'. If all A, B and C reacted with reagent and have 'n' factor [n factor; eq. wt. = mol. wt./n] in the ratio of 1:2:3 with the reagent. The k in terms of t, n_1 and n_2 is:

(a) $k=\frac{1}{t}\ln\left(\frac{n_2}{n_2-n_1}\right)$ (b) $k=\frac{1}{t}\ln\left(\frac{2n_2}{n_2-n_1}\right)$

(c) $k=\frac{1}{t}\ln\left(\frac{4n_2}{n_2-n_1}\right)$ (d) $k=\frac{1}{t}\ln\left(\frac{4n_2}{5(n_2-n_1)}\right)$

20. The gaseous decomposition reaction, $A(g) + 2B(g) \rightarrow C(g)$ is observed to first order over the excess of liquid water at 25°C. It is found that after 10 minutes the total pressure of system is 188 torr and after very long time it is 388 torr. The rate constant of the reaction (in hr^{-1}) is:

(a) 0.02 (b) 1.2

(c) 0.2 (d) none of these

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Answers

1. (a) 2. (d) 3. (a) 4. (d) 5. (c) 6. (a) 7. (b) 8. (a) 9. (c) 10. (c) 11. (c) 12. (c) 13. (c) 14. (a) 15. (c) 16. (c) 17. (b) 18. (c) 19. (d) 20. (b)

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CHEMICAL KINETICS

DPP-4

1. For a second order reaction A+ B $\rightarrow$ products, where the initial concentration of the reactants are the same (x mol/lit) and k is the rate constant, the half life of the reaction is :

   (a) 1/kx (b) 0.693 K

   (c) 0.5/k (d) 0.5 kx

2. For a first order reaction, the half-life is 50s. Identify the correct statement from the following.

   (a) The reaction is complete in 100 s

   (b) The reaction begins after 50 s

   (c) The same quantity of A is consumed for every 50 s of the reaction.

   (d) Quantity of A remaining after 100 s is half of what remains after 50 s.

3. If the concentration vs time plot is found to be linear with a negative slope, the order of the reaction is:

   (a) 0 (b) 1

   (C) 2 (d) Cannot be determined

4. Consider the plots for the types of reaction, nA $\rightarrow$ B + C

   These plots respectively correspond to the reaction orders :

   (a) 0, 2, 1 (b) 0, 1, 2

   (c) 1, 1, 2 (d) 1, 0, 2

5. If the concept of half-life is generalized to quarter-life of a first order chemical reaction, it will be equal to

   (a) $\frac{\ln 2}{k}$ (b) $\frac{\ln 4}{k}$

   (c) $\frac{4}{k}$ (d) $\frac{1}{4k}$

6. For a first order reaction A $\rightarrow$ products, the plot of $\ln\left(\frac{|A|_n}{|A|_0}\right)$ vs time, where $[A]_0$ and $[A]_t$ refer to concentration at time t = 0 and t respectively, is

   (a) a straight line with a positive slope passing through origin

   (b) a straight line with a negative slope passing through origin

   (c) an exponential curve asymptotic to the time axis

   (d) an exponential curve symptotic to the time axis

7. For a reaction, 2A + B $\rightarrow$ 3Z, if the rate of consumption of A is 2×10^{-1} mol dm^{-3} s^{-1} the rate of formation of Z (in mol dm^{-3} s^{-1}) will be

(a) 3×10^{-4} (b) 2×10^{-4}

(c) $\frac{4}{3} \times 10^{-4}$ (d) 4×10^{-4}

8. Half-life $t_{1/2}$ for a third order reaction 3C $\rightarrow$ products, where C_0 is the initial concentration of C, will be

(a) $\frac{3}{2kC_0^2}$ (b) $\frac{1}{kC_0}$

(c) $\frac{3}{2kC_0}$ (d) $\frac{2}{2kC_0^2}$

9. In kinetic study of a chemical reaction, slopes are drawn at different times in the plot of concentration of reactants versus time. The magnitude of slope with increase of time

(a) remains unchanged

(b) increases

(c) decreases

(d) increases and decreases periodically

10. If the unit of the rate constant of a reaction is $L^3mol^{-3}s^{-1}$, the order of the reaction is

(a) 1 (b) 2

(c) 3 (d) 4

11. For a given first order reaction, the reactant reduces to 1/4th to its initial value in 10 minutes. The rate constant of the reaction is :

(a) 0.1386 min^{-1}

(b) 0.0693min^{-1}

(c) 0.1386 mol L^{-1} min^{-1}

(d) 0.0693 mol L^{-1} min^{-1}

12. In the following reaction A$\rightarrow$B+C, rate constant is 0.001 Ms^{-1}. If we start with 1 M of A then conc. Of A and B after 10 minutes are respectively

(a) 0.5 M, 0.5 M (b) 0.6 M, 0.4 M

(c) 0.4 M, 0.6 M (d) None of these

13. For the reaction $2X_3 = 3X_2$, the rate of formation of X_2 is :

(a) $3\left(-d[X_3]/dt\right)$ (b) $\frac{1}{2}\left(-d[X_3]/dt\right)$

(c) $\frac{1}{3}\left(-d[X_3]/dt\right)$ (d) $\frac{3}{2}\left(-d[X_3]/dt\right)$

14. For the reaction : $Br_2(g) + BF_2(g) \rightarrow 2BrF_3(g)$, the equilibrium constant at 2000 K and 1.0 bar is 5.25. When the pressure is increased by 8-fold, the equilibrium constant.

(a) Increase by a factor of 1.86

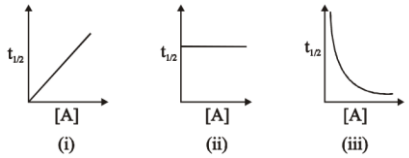
(b) Decrease by a factor of 1.86

(c) Remains same

(d) Increases by a factor of 8

15. Consider the plots, gives below, for the types of reaction:

$nA \rightarrow B + C$



These plots respectively correspond to the reaction orders :

(a) 0, 1, 2 (b) 1, 2, 0

(c) 1, 0, 2 (d) None of these

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Answers

1. (a) 2. (d) 3. (a) 4. (d) 5. (b) 6. (b) 7. (a) 8. (a) 9. (c) 10. (d) 11. (a) 12. (c) 13. (a) 14. (c) 15. (c)

QUANTA CHEMISTRY

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CHEMICAL KINETICS

DPP-5

1. In the reaction between NO and H_2 the following data are obtained

   Experiment I : P_{HP} = constant

P_{NO} (mm of Hg)	359	300	152
$\frac{-dP_{NO}}{dt}$	1.50	1.03	0.25

   Experiment II : P_{NO} = constant

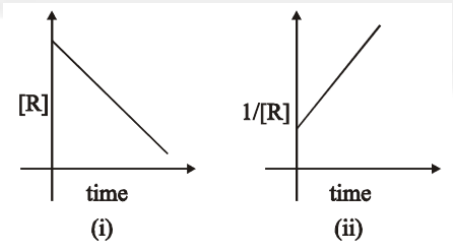
P_{H_2} (mm of Hg)	289	205	147
$\frac{-dP_{H_2}}{dt}$	1.60	1.10	0.79

   The order with respect to H_2 and NO are

   (a) 1 with respect to NO and 2 with respect to H_2 (b) 2 with respect to NO and 1 with respect to H_2

   (c) 1 with respect to NO and 3 with respect to H_2 (d) 2 with respect to NO and 2 with respect to H_2

2. The concentration of a reactant R varies with time for two different reactions as shown in the following plots :



   The orders of these two reactions I and II, respectively are

   (a) 0, 3 (b) 2, 0

   (c) 0, 2 (d) None of these

3. If the rates of a reaction are R_1 and R_2 at concentrations C_1 and C_2 of a reactant respectively, the order of reaction, 'n' (assuming that the concentrations of all other reactants and T remains constant) with respect to that reactant is given by

(a) $n=\frac{\log R_1-\log R_2}{\log C_1-\log C_2}$ (b) $n=\frac{\log C_1-\log C_2}{\log R_1-\log R_2}$

(c) $n=\frac{\log C_1-\log R_1}{\log C_2-\log C_1}$ (d) $n=\frac{\log C_2-\log R_2}{\log C_1-\log C_2}$

4. The fractions of groups condensed at time t in any stepwise condensation polymerization (overall second order) reaction is

(a) $1 + kt [A]_0$ (b) $\frac{1}{1+kt[A]_0}$

(c) $\frac{kt[A]_0}{1+kt[A]_0}$ (d) $\frac{1+k[A]_0}{kt[A]_0}$

5. Reaction between A and B is carried out for different initial concentrations and the corresponding half-life times are measured. The data listed in the table :

The rate can be prepared as

(a) $k [A][B]$ (b) $k[A]^2$

(c) $k[A]^2[B]^2$ (d) $k[A][B]^2$

6. For the reaction P + Q + R + S, $\longrightarrow$, experimental data for the measured initial rates is given below.

Expt.	Initial conc. P (M)	Initial conc. Q (M)	Initial conc. R (M)	Initial rate (Ms^{-1})
1	0.2	0.5	0.4	8.0×10^{-5}
2	0.4	0.5	0.4	3.2×10^{-4}
3	0.4	2.0	0.4	1.28×10^{-3}
4	0.1	0.25	1.6	4.0×10^{-5}

The order of the reaction with respect to P, Q and R respectively is :

(a) 2, 2, 1 (b) 2, 1, 2

(c) 2, 1, 1 (d) 1, 1, 2

7. The half-life of first order of decomposition of NH_4NO_2 is 2.1 hr at 288 K temperature $NH_4NO_2(aq) \rightarrow N_2O(g) + H_2O$ (aq), if 6.2g of NH_4NO_2 is allowed to decompose. The time required for NH_4NO_2 to decompose 90% and the volume of dry N_2O produced at this point measured at STP are respectively :

(a) 6.978 hr, 2.016 L (b) 0.319 hr, 2.15 L

(c) 0.319 hr, 2.016 L (d) None of these

8. For a first order homogenous gaseous reaction $A \rightarrow 2B + C$ then initial pressure was P_i while total pressure after 't' was P_t. The write expression for the rate constants k in terms of P_i, P_t and t is:

(a) $k=\frac{2.303}{t}\log\left(\frac{2P_i}{3P_i-P_i}\right)$ (b) $k=\frac{2.303}{t}\log\left(\frac{2P_i}{3P_t-P_i}\right)$

(c) $k = \frac{2.303}{t}\log\left(\frac{P_i}{P_i - P_t}\right)$ (d) None of these

9. The half-life ($t_{1/2}$) for the hydrolysis of an ester varies with the initial concentration of the reactant ($[E_0]$) as follows :

$[E_0]_0 / 10^{-2}\,mol\,L^{-1}$	5.0	4.0	3.0
$t_{1/2}/s$	240	300	400

The order of the reaction is:

(a) 0 (b) 1

(c) 2 (d) 3

10. The half-life for a reaction at initial concentrations of 0.1 and 0.4 mol^{-1} are 200 s and 50 s respectively. The order of the reaction is

(a) 0 (b) 1

(c) 2 (d) 3

11. Sucrose is converted to a mixture of glucose and fructose is a pseudo first order process under alkaline conditions. The reactions has a half-life of 28.4 min. The time required for the reduction of a 8.0 mM sample of sucrose to 1.0 mM is

(a) 56.8 min (b) 170.4 min

(c) 85.2 min (d) 227.2 min

12. Decomposition of ammonia on tungsten at 850°C has a rate constant value of 0.10 Torr s^{-1}. If the initial pressure of ammonia is 100 Torr, the pressure of ammonia (in Torr at t = 200 s is

(a) 10 (b) 20

(c) 50 (d) 80

13. A substance A is consumed by a reaction of unknown order. The initial concentrations is 1mM, and concentrations at later times are as shown :

Time (min)	[A] (mM)
1	0.83
2	0.72
4	0.56
8	0.38
16	0.24

What is the order of the reaction?

(a) zero (b) first-order

(c) second-order (d) pseudo-first order

14. The method of initial rates is used to determine the rate law for the reaction given below.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

The following initial rates were determined at the given partial pressures(p) of reactants.

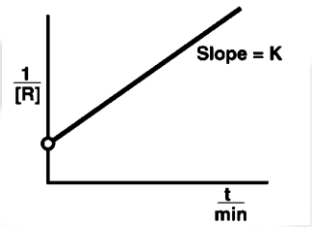
pNO(mmHg)	PH_2(mmHg)	Initial rate (M/min)
200	400	0.46
400	200	0.92
400	400	1.85

These data imply which of the following rate laws?

(a) $\text{rate} = kp^2_{NO}p^2H_2$ (b) $\text{rate} = kp^2_{NO}pH_2$

(c) $\text{rate} = kp_{NO}p^2H_2$ (d) $\text{rate} = kp_{NO}pH_2$

15. The graph below plots the progress of a dimerization reaction involving species A it depicts a straight line with slope k (the rate constant). What is the value of the intercept, c in the graph?



(a) $[A_{(0)}]$ (b) $[A_{(0)}]^2$

(c) $[A_{(0)}]^{-1}$ (d) k x $[A_{(0)}]^2$

• • • • •

Answers

1. (b) 2. (c) 3. (a) 4. (c) 5. (c) 6. (c) 7. (a) 8. (a) 9. (c) 10. (c) 11. (c) 12. (d) 13. (c) 14. (b) 15. (c)

QUANTA CHEMISTRY

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CHEMICAL KINETICS

DPP-6

1. Experimentally determined rate law for the chemical reaction,

   $2NO_2F \rightarrow 2NO_2 + F_2$ is $R = k[NO_2F]$

   The rate determining step consistent with the rate law is

   (a) $2NO_2F \rightarrow 2NO_2 + F_2$ (b) $NO_2F + F \rightarrow NO_2 + F_2$

   (c) $NO_2F \rightarrow NO_2 + F$ (d) $NO_2F + F \rightarrow NO_2F$

2. Which of the following relation is correct for k_f and k_b in an equilibrium process that contains equal moles of reactants and products.

   (a) $k_f = k_b$ (b) $k_f > k_b$

   (c) $k_f < k_b$ (d) We cannot predict

3. Listed in the table are forward and reverse rate constants for the reaction :

   $2NO_1(g) \rightleftharpoons N_2(g) + O_2(g)$

Temperature(K)	$k_f(M^{-1}S^{-1})$	$k_b\left(M^{-1}S^{-1}\right)$
1400	0.29	1.1×10^{-6}
1500	1.3	1.4×10^{-5}

   Select the correct statements :

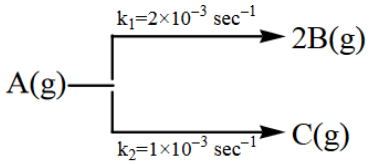
   (a) Reaction is exothermic and value of equilibrium constant (K_{eq}) at 1400 K is 3.79×10^{-6}.

   (b) Reaction is endothermic and value of K_{eq} at 1400 K is 2.63×10^5

   (c) Reaction is exothermic and value of Keq at 1400 K is 2.63×10^5

   (d) Reaction is endothermic and value of Keq at 1500 K is 9.28×10^5

4. A decomposes as,



the rate of appearance of B, taking 2M concentration of A at any time 't', is equal to :

(a) 2×10^{-3} Ms^{-1} (b) 4×10^{-3} Ms^{-1}

(c) 8×10^{-3} Ms^{-1} (d) None of these

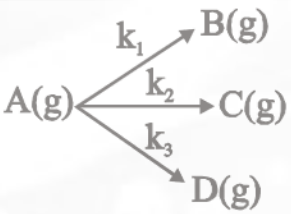
5. In a consecutive first order reaction, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

(where k_1 and k_2 are the respective rate constants) species B has transient existence. Therefore,

(a) $k_1 \approx k_2$ (b) $k_1 = 2k_2$

(c) $k_1 >> k_2$ (d) $k_1 << k_2$

6. A gaseous compound A reacts by three independent first order processes (as shown in figure) with rate constant 2×10^{-3}, 3×10^{-3} and 1.93×10^{-3} sec^{-1} for products B, C and D respectively. If initially pure A was taken in a closed container with P=8 atm, then the partial pressure of B (in atm) after 100 sec from start of experiment.



(a) 0.288 (b) 0.577

(c) 1.154 (d) none of these

7. For the following chemical reaction

$A \xrightarrow{k_1} B$

$A \xrightarrow{k_2} B$

$B \xrightarrow{k_3} C$

$C \xrightarrow{k_4} B$

The rate constant k_1 and k_2 are at least 1000 times slower than either k_3 or k_4. During the course of the above reactions the ratio of the products B and C will be

(a) [B] / [C] = k_3 / k_4 (b) [B] / [C] = k_4 / k_3

(c) [B] / [C] = k_2 / k_3 / k_1k_4 (d) [B] / [C] = k_1 / k_2

8. In the following reaction mechanism

$NO_2(g) + F_2(g) \rightarrow NO_2(g) + F(g)$ .....(1)

$F(g) + NO_2(g) \rightarrow NO_2F(g)$ .....(2)

the first step, having a rate constant K_1, is very slow while the second step having a rate constant K_2, is very first. The rate law for this mechanism will therefore be

(a) Rate = $k_1[NO_2][F_2]$ (b) Rate = $k_1k_2[NO_2]_2[F_2]^2$

(c) Rate = $k_2[F][NO_2]$ (d) Rate = $k_2[NO_2F][F]$

9. Examine the following first order consecutive reactions. The rate constant (in s^{-1} units) for each step is given above the arrow mark

(A) $P \xrightarrow{10^5} Q \xrightarrow{10^8} R$ (B) $P \xrightarrow{10^5} Q \xrightarrow{10^3} R$

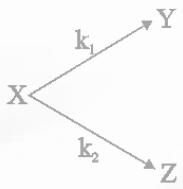
(C) $P \xrightarrow{10^7} Q \xrightarrow{10^7} R$ (D) $P \xrightarrow{10^2} Q \xrightarrow{10^6} R$

Steady-state approximate can be applied t.o

(a) Atony (b) C only

(c) B and C only (d) A and D only

10. For the parallel first order reaction shown below:



the value of k_1 is $1 \times 10^{-1}s^{-1}$. If the reaction starts from X, the ratio of the concentrations of Y and Z at any given tune during the course of the reaction is found to be $\frac{[Y]}{[Z]} = \frac{1}{4}$

The value of k_2 is :

(a) $1 \times 10^{-4}s^{-1}$ (b) $2.5 \times 10^{-5}s^{-1}$

(c) $4 \times 10^{-4}s^{-1}$ (d) $4 \times 10^{4}s^{-1}$

• • • • •

Answers

1. (c) 2. (d) 3. (c) 4. (c) 5. (a) 6. (c) 7. (d) 8. (a) 9. (d) 10. (c)

QUANTA CHEMISTRY

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CHEMICAL KINETICS

DPP-7

Common data for Q.1 and Q.2

For the opposing reaction, $A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C + D$

The forward reaction has values E_2 = 100 kJ mol^{-1} and A = 1.0 × 1010 $M^{-1}s^{-1}$. The equilibrium concentration of A, B, C and D are 1.0M, 2.0M, 5.0M and 4.0M respectively, at 700 K.

1. The values of k_1 and k_{-1}, respectively, at this temperature are

   (a) 20 $M^{-1}s^{-1}$ and 2.0 $M^{-1}s^{-1}$ (b) 345 $M^{-1}s^{-1}$ and 34.5 $M^{-1}s^{-1}$

   (c) 34.5 $M^{-1}s^{-1}$ and 3.45 $M^{-1}s^{-1}$ (d) 200 $M^{-1}s^{-1}$ and 20 $M^{-1}s^{-1}$

2. The rate constant (k_1) for the forward reaction 1000 K is :

   (a) 5.98 × 10^4 M^{-1} min^{-1} (b) 5.98 × 10^2 M^{-1} s^{-1}

   (c) 1.00 × 10^3 M^{-1} s^{-1} (d) 5.98 × 10^4 M^{-1} s^{-1}

3. For the reaction of the type $P \xrightarrow{k_1} Q \xrightarrow{k_2} R$, given that $[P]_0$ = 1.0 M; k_1 = 1 × 10^{-3} s^{-1} and k_2 = 1 × $10^{-4}s^{-1}$, the time at which the concentrations of Q and R are 0.5966 M and 0.355M, respectively, is

   (a) 500s (b) 750s

   (c) 1000s (d) 1500s

4. Consider an exothermic reaction, $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} I$ as the temperature increases

   (a) k_1 , k_{-1}, and k_1 /k_{-1} increases

   (b) k_1 increases, k_{-1} decreases, and k_1 /k_{-1} increases

   (c) k_1, k_{-1} increases and k_1 /k_{-1} decreases

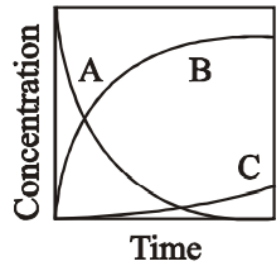
   (d) k_1 and k_{-1} decrease, and k_1 /k_{-1} increases

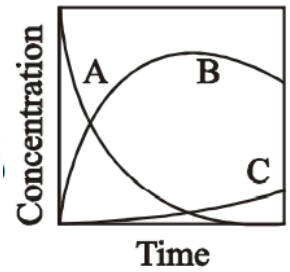
5. A reaction proceeds through the formation of an intermediate B in an unimolecular reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$. The integrated rate law for this reaction is

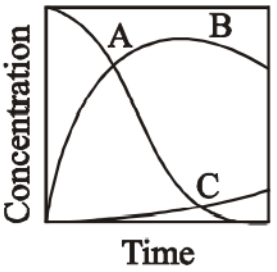
   (a) $[A] = [A]_0 e^{-k_a t}$ (b) $[A] = [A]_0 \left(e^{-k_a/t} - e^{-k_b/t}\right)$

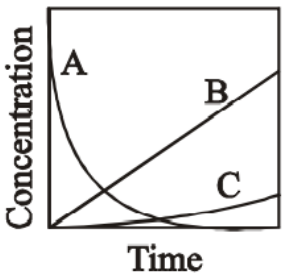
(c) $[A]=\frac{[A]_0}{2}\left(1+\frac{k_a e^{k_b t}-k_b e^{-k_a t}}{k_a-k_b}\right)$ (d) $[A]=[A]_0\left(1+e^{-k_a t}-e^{-k_a t}\right)$

6. If $k_a >> k_b$, then concentration vs. time plot for the above reaction is :

(a) 

(b) 

(c) 

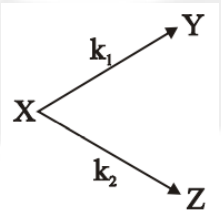
(d) 

7. For a reaction of the type $X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Y$, the correct rate expression is ($[X]_0$ and [X] corresponds to the concentration of X at time t = 0 and t =t, respectively)

(a) $-\frac{d[X]}{dt}=k_1[X]_0-(k_1+k_2)[X]$ (b) $-\frac{d[X]}{dt}=(k_1+k_2)[X]-k_2[X]_0$

(c) $-\frac{d[X]}{dt}=(k_1+k_2)[X]_0-k_1[X]$ (d) $-\frac{d[X]}{dt}=(k_1-k_2)[X]-k_1[X]_0$

8. For the parallel first order reaction shown below

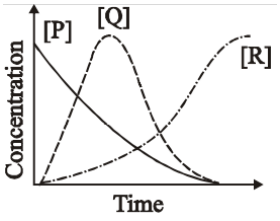


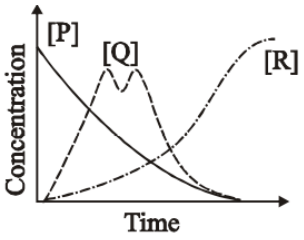
the value of k_1 is $1 \times 10^{-1} s^{-1}$. If the reaction starts from X, the ratio of the concentrations of Y and Z at any given time during the course of the reaction is found to be $\frac{[Y]}{[Z]}=\frac{1}{4}$. The value of k_2 is :

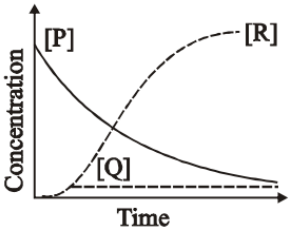
(a) $1 \times 10^{-4} s^{-1}$ (b) $2.5 \times 10^{-5} s^{-1}$

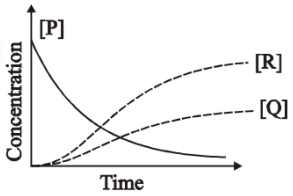
(c) $4 \times 10^{-4}\ s^{-1}$ (d) $4 \times 10^{4}\ s^{-1}$

9. For the first order consecutive reaction, $P \rightarrow Q \rightarrow R$, under steady state approximation to [Q], the variation of [P], [Q] and [R] with time are best represented by

(a) 

(b) 

(c) 

(d) 

10. For the following consecutive first order reactions

$$X \xrightarrow{K_1=2.0s^{-1}} Y \xrightarrow{K_1=0.1s^{-1}} Z$$

the time (in seconds) required for Y to reach its maximum concentration (assuming only X is present at time t = 0) is _____ (unto two decimal places)

• • • • •

Answers

1. (b) 2. (c) 3. (c) 4. (cv) 5. (c) 6. (a) 7. (d) 8. (a) 9. (b) 10. (b)

QUANTA CHEMISTRY

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CHEMICAL KINETICS

DPP-8

1. Experimentally determined rate law for the chemical reaction,

   $2NO_2F \rightarrow 2NO_2 + F_2$ is $R = k[NO_2F]$

   The rate determining step consistent with the rate law is

   (a) $2NO_2F \rightarrow 2NO_2 + F_2$ (b) $NO_2F + F \rightarrow NO_2 + F_2$

   (c) $NO_2F \rightarrow NO_2 + F$ (d) $NO_2F + F \rightarrow NO_2F$

2. Which of the following relation is correct for k_f and k_b in an equilibrium process that contains equal moles of reactants and products.

   (a) $k_f = k_b$ (b) $k_f > k_b$

   (c) $k_f < k_b$ (d) We cannot predict

3. Listed in the table are forward and reverse rate constants for the reaction :

   $2NO_3(g) \rightleftharpoons N_2(g) + O_2(g)$

Temperature(K)	$k_f(M^{-1}S^{-1})$	$k_b(M^{-1}S^{-1})$
1400	0.29	1.1×10^{-6}
1500	1.3	1.4×10^{-5}

   Select the correct statements :

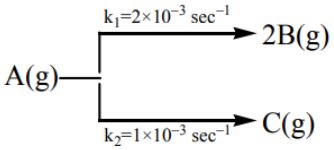
   (a) Reaction is exothermic and value of equilibrium constant (K_{eq}) at 1400 K is 3.79×10^{-6}.

   (b) Reaction is endothermic and value of K_{eq} at 1400 K is 2.63×10^5

   (c) Reaction is exothermic and value of K_{eq} at 1400 K is 2.63×10^5

   (d) Reaction is endothermic and value of K_{eq} at 1500 K is 9.28×10^5

4. A decomposes as



   the rate of appearance of B, taking 2M concentration of A at any time 't', is equal to :

(a) 2×10^{-3} Ms^{-1} (b) 4×10^{-3} Ms^{-1}

(c) 8×10^{-3} Ms^{-1} (d) None of these

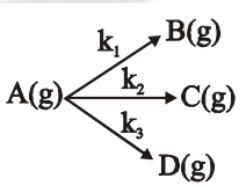
5. In a consecutive first order reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

(where k_1 and k_2 are the respective rate constants) species B has transient existence. Therefore,

(a) $k_1 \approx k_2$ (b) $k_1 = 2k_2$

(c) $k_1 >> k_2$ (d) $k_1 << k_2$

6. A gaseous compound A reacts by three independent first order processes (as shown in figure) with rate constant 2×10^{-3}, 3×10^{-3} and 1.93×10^{-3} sec^{-1} for products B, C and D respectively. If initially pure A was taken in a closed container with P=8 atm, then the partial pressure of B (in atm) after 100 sec from start of experiment.



(a) 0.288 (b) 0.577

(c) 1.154 (d) none of these

7. For the following chemical reaction

$A \xrightarrow{k_1} B$

$A \xrightarrow{k_2} B$

$B \xrightarrow{k_3} C$

$C \xrightarrow{k_4} B$

The rate constant k_1 and k_2 are at least 1000 times slower than either k_3 or k_4. During the course of the above reactions the ratio of the products B and C will be

(a) [B] / [C] = k_3 / k_4 (b) [B] / [C] = k_4 / k_3

(c) [B] / [C] = k_2k_3 / k_1k_4 (d) [B] / [C] = k_1 / k_2

8. In the following reaction mechanism

$NO_2(g) + F_2(g) \rightarrow NO_2(g) + F(g)$ .....(1)

$F(g) + NO_2(g) \rightarrow NO_2F(g)$ .....(2)

the first step, having a rate constant K_1, is very slow while the second step having a rate constant K_2, is very first. The rate law for this mechanism will therefore be

(a) Rate = $k_1[NO_2][F_2]$ (b) Rate = $k_1k_2[NO_2]_2[F_2]^2$

(c) Rate = $k_2[F][NO_2]$ (d) Rate = $k_2[NO_2F][F]$

9. Examine the following first order consecutive reactions. The rate constant (in s^{-1} units) for each step is given above the arrow mark

(A) $P \xrightarrow{10^5} Q \xrightarrow{10^8} R$ (B) $P \xrightarrow{10^5} Q \xrightarrow{10^3} R$

(C) $P \xrightarrow{10^7} Q \xrightarrow{10^7} R$ (D) $P \xrightarrow{10^2} Q \xrightarrow{10^6} R$

Steady-state approximate can be applied to

(a) A only (b) C only

(c) B and C only (d) A and D only

10. In a consecutive first order reaction, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

(where k_1 and k_2 are the respective rate constants) species B has transient existence. Therefore,

(a) $k_1 \approx k_2$ (b) $k_1 = 2k_2$

(c) $k_1 >> k_2$ (d) $k_1 << k_2$

Common data for Q.11 and Q.12

For the opposing reaction, $A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C + D$

The forward reaction has values E_2 = 100 kJ mol^{-1} and A = 1.0×10^{10} $M^{-1}s^{-1}$. The equilibrium concentration of A, B, C and D are 1.0M, 2.0M, 5.0M and 4.0M respectively, at 700 K.

11. The values of k_1 and k_{-1}, respectively, at this temperature are

(a) 20 $M^{-1}s^{-1}$ and 2.0 $M^{-1}s^{-1}$ (b) 345 $M^{-1}s^{-1}$ and 34.5 $M^{-1}s^{-1}$

(c) 34.5 $M^{-1}s^{-1}$ and 3.45 $M^{-1}s^{-1}$ (d) 200 $M^{-1}s^{-1}$ and 20 $M^{-1}s^{-1}$

12. The rate constant (k_1) for the forward reaction 1000 K is :

(a) 5.98×10^4 M^{-1} min^{-1} (b) 5.98×10^2 M^{-1} s^{-1}

(c) 1.00×10^3 M^{-1} s^{-1} (d) 5.98×10^4 M^{-1} s^{-1}

13. For the reaction of the type $P \xrightarrow{k_1} Q \xrightarrow{k_2} R$, given that $[P]_0$ = 1.0 M; $k_1 = 1 \times 10^{-3}$ s^{-1} and $k_2 = 1 \times 10^{-4} s^{-1}$, the time at which the concentrations of Q and R are 0.5966 M and 0.355M, respectively, is

(a) 500s (b) 750s

(c) 1000s (d) 1500s

14. Consider an exothermic reaction, $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} I$ as the temperature increases

(a) k_1 , k_{-1}, and k_1 / k_{-1} increases

(b) k_1 increases, k_{-1} decreases, and k_1 / k_{-1} increases

(c) k_1, k_{-1} increases and k_1 / k_{-1} decreases

(d) k_1 and k_{-1} decrease, and k_1 / k_{-1} increases

15. A reaction proceeds through the formation of an intermediate B in an unimolecular reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$. The integrated rate law for this reaction is

(a) $[A]=[A]_0 e^{-k_a t}$

(b) $[A]=[A]_0\left(e^{-k_a/t}-e^{-k_b/t}\right)$

(c) $[A]=\frac{[A]_0}{2}\left(1+\frac{k_a e^{k_b t}-k_b e^{-k_a t}}{k_a-k_b}\right)$

(d) $[A]=[A]_0\left(1+e^{-k_a t}-e^{-k_a t}\right)$

•••••

Answers

1. (c) 2. (d) 3. (c) 4. (c) 5. (a) 6. (c) 7. (d) 8. (a) 9.(d) 10.(a) 11.(b) 12.(c) 13.(c) 14.(c) 15.(c)

QUANTA CHEMISTRY

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CHEMICAL KINETICS

DPP-9

1. Which of the following statements is NOT correct for a catalyst?

   (a) It increases the rate of a reaction.

   (b) It is not consumed in the course of a reaction.

   (c) It provides an alternative pathway for the reaction.

   (d) It increases the activation energy of the reaction.

2. A catalyst increases the rate of a reaction by:

   (a) making the enthalpy of reaction negative.

   (b) making the Gibbs free energy of reaction negative

   (c) reducing the activation energy of the reaction

   (d) increasing the entropy change m the reaction.

3. For an enzyme-substrate reaction the Michaelis constant is 0.042 mol dm^{-3}. The rate of this reaction is 2.45×10^{-5} mol dm^{-3} s^{-1} when the substrate concentration is 0.89 mol dm^{-3}. The maximum velocity of this enzymolysis is

   (a) 2.57×10^{-5} mol dm^{-3} s^{-1} (b) 2.45×10^{-5} mol dm^{-3} s^{-1}

   (c) infinite (d) 1.31×10^{-5} mol dm^{-3} s^{-1}

4. The speed of a reaction that involves an enzyme increases are

   (a) Temperature decreases (b) pH becomes less than optimal

   (c) Substrate concentration increases (d) All of the above

5. In a homogeneous catalytic reaction, 1.0 M of a substance and 1.0 μM of a catalyst yields 1.0 mM of a product in 10 seconds. The turnover frequency (TOF) of the reaction (s^{-1}) is:

   (a) 10^{-2} (b) 10^{2}

   (c) 10^{-3} (d) 10^{3}

6. For an enzyme catalyzed reaction, a Lineweaver-Burk plot gave the following data:

   slope = 40s intercept = 4 (mmol dm^{-3} $s^{-1})^{-1}$. If the initial concentration of enzyme is 2.5×10^{-9} mol dm^{-3}, what is the catalytic efficiency (in dm^3 $mol^{-1}s^{-1}$) of the reaction?

(a) 10^5 (b) 10^6

(c) 10^7 (d) 10^4

7. In the Michaelis-Menten mechanism for enzyme kinetics, the expression obtained is

$$\frac{v}{[E]_0[S]} = 1.41\times10^{12} - \frac{10^4 v}{[E]_0}$$

The values of k_3 (k_{exp}, mol L^{-1} s^{-1} and K (Michaelis constant, mol L^{-1}), respectively are

(a) 1.4×10^{12}, 10^4 (b) 1.4×10^8 , 10^4

(c) 1.4×10^8 , 10^{-4} (d) 1.4×10^{12}, 10^{-2}

8. In the Lineweaver-Burk plot of (initial rate)$^{-1}$ vs. (initial substrate concentration)$^{-1}$ for an enzyme catalyzed reaction following Michaelis-Menten mechanism, the y-intercept is 5000 M^{-1} s. If the initial enzyme concentration 1×10^{-9} M, the turnover number is

(a) 2.5×10^3 (b) 1.0×10^4

(c) 2.5×10^4 (d) 2.0×10^5

9. v_{max} and K_m for an enzyme catalyzed reaction are 2.0×10^{-3} Ms^{-1} and 1.0×10^{-6} M, respectively. The rate of the reaction when the substrate concentration is 1.0×10^{-6} M is

(a) 3.0×10^{-3} s^{-1} (b) 1.0×10^{-3} s^{-1}

(c) 2.0×10^{-3} s^{-1} (d) 0.5 s^{-1}

10. For an enzyme-substrate reaction, a plot between 1/v and $1/[S]_0$ yields a slope of 40 s. If the enzyme concentration is 2.5 μM, then the catalytic efficiency of the enzyme is

(a) 40 $Lmol^{-1}$ s^{-1} (b) 10^{-4} $Lmol^{-1}$ s^{-1}

(c) 10^7 $Lmol^{-1}$ s^{-1} (d) 104 $Lmol^{-1}$ s^{-1}

11. In an enzyme-catalysed reaction $E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P$, $k_2 = 3.42 \times 10^4$ s^{-1}. If $[E]_0 = 1 \times 10^{-2}$ mol dm^{-3}, the magnitude of maximum velocity and turn over number using Michaelis-Menten kinetics are

(a) 3.42×10^2 mol $dm^{-3}s^{-1}$; 3.42×10^4 s^{-1} (b) 3.42×10^6 mol $dm^{-3}s^{-1}$; 3.42×10^4 s^{-1}

(c) 3.42×10^4 mol $dm^{-3}s^{-1}$; 3.42×10^6 s^{-1} (d) 3.42×10^4 mol dm^{-3} s^{-1}; 3.42×10^2 s^{-1}

12. The slope and intercept obtained from (1/Rate) against (1/substrate concentration) of an enzyme catalyzed reaction are 300 and 2×10^5, respectively. The Michaelis-Menten constants of the enzyme in this reaction is

(a) 5×10^6 M (b) $5 \times M^{-6}$ M′

(c) 1.5×10^3 M (d) 1.5×10^{-3} M

13. For an enzyme-substrate reaction : $E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES; ES \xrightarrow{k_2} E + P$, the slope and the intercept of the plot between 1/r and 1/[S] are 10^{-2} s and 102 M^{-1} s, respectively. If $E_0 = 10^{-6}$ M and $\frac{k_{-1}}{k_2} = 1000$, the value of k_1 will be close to (in units of M^{-1} s^{-1}) [r is the rate of the reaction, E_0 is the initial concentration of the enzyme)

(a) 1×10^{11} (b) 1×10^{4}

(c) 1×10^{8} (d) 1×10^{6}

14. The mechanism of enzyme (E) catalysed reaction of a substrate (S) to yield product (P) is:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [ES] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + P; \qquad \frac{-d[S]}{dt} = \frac{k_1 k_2 [S]_0 + k_2 k_{-2} [P]}{k_1 [S]_0 + k_{-2} [P] + k_{-1} + k_2} [E]_0$$

If a small amount of S is converted to P, the maximum rate for the reaction will be observed for

(a) $(k_1 + k_2) >> k_1[S]_0$ (b) $(k_{-1} + k_2) << k_1[S]_0$

(c) $(k_1 + k_2) >> k_1[S]_1$ (d) $k_{-2} << k_1$

15. Under physiological conditions, the conversion of CO_2 to bicarbonate ion by carbonic anhydrase enzyme (MW = 30,000 g mol^{-1}) has a turnover number of 4.00×10^5 s^{-1}. The minimum amount of enzyme (in μg) required to convert 0.44 g of CO_2 to bicarbonate ions in 100 seconds is _____ (up to two decimal places)

• • • • •

Answers

1. (d) 2. (c) 3. (a) 4. (c) 5. (b) 6. (c) 7. (c) 8. (d) 9.(b) 10.(d) 11.(a) 12.(d) 13.(a) 14.(b)

15.(7.40 to 7.60)

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CHEMICAL KINETICS

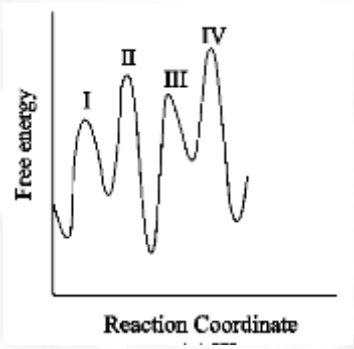
DPP-10

1. For an endothermic reaction where ΔH represents the enthalpy of reaction is kJ/mol, the minimum value for the energy of activation will be :

   (a) less than ΔH (b) more than ΔH

   (c) equal to ΔH (d) zero

2. Identify the transition state which determines the rate of the reaction from the free energy diagram.

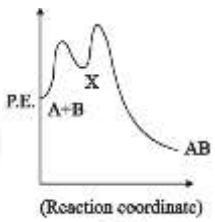


   (a) I (b) II

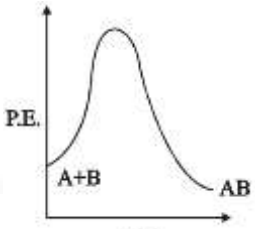
   (c) III (d) IV

3. For an exothermic chemical process occurring in two steps as follows:

   (i) $A + B \rightarrow X$ (slow) (ii) $X \rightarrow AB$ (fast) The process of reaction can be best describe by

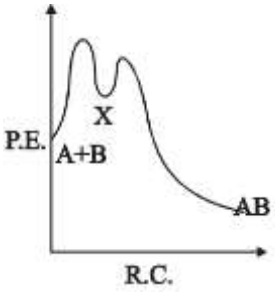


(a)

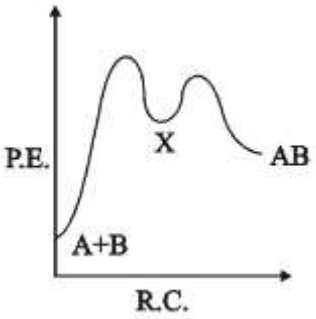


(b)

(c)

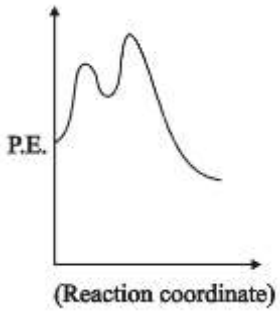


(d)

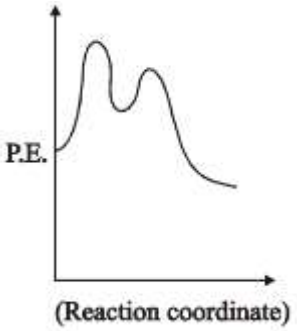


4. Select the correct diagram for an endothermic reaction that proceeds through two steps, with the second step is rate determining :

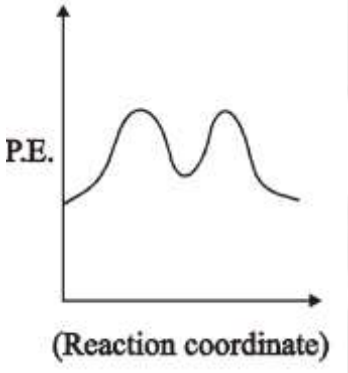
(a)



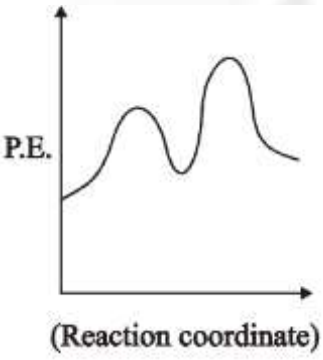
(b)



(c)



(d)



5. The plot of ln k versus 1/T is linear with slope of

(a) $-E_a / R$ (b) E_a / R

(c) $E_a / 2.303\ R$ (d) $-E_a / 2.303R$

6. For a complex reaction : $A \xrightarrow{K} \text{products}$

E_{a1} = 180 kJ/mol ; E_{a2} = 80 kJ/mol ; E_{a3} = 50 kJ/mol

Overall rate constant k is related to individual rate constant by the equation $K = \left(\frac{k_1 k_2}{k_3}\right)^{2/3}$

Activation energy (k_j/mol) for the overall reaction is :

(a) 100 (b) 43.44

(c) 150 (d) 140

7. The temperature coefficient of a reaction is :

(a) The rate constant

(b) The rate constant at a fixed temperature

(c) The ratio of rate constant at two temperature

(d) The ratio of rate constant differing by 10°C preferably k_{308} / k_{298}

8. A first order reaction is 50% completed in 20 minutes at 27°C and in 5 minutes at 47°C. The energy of activation of the reaction is :

(a) 43.85 kJ/mol (b) 55.14 kJ/mol

(c) 11.97 kJ/mol (d) 6.65 kJ/mol

9. A catalyst lowers the activation energy for a certain reaction from 83.314 to 75 kJ mol^{-1} at 500 K. What will be the rate of reaction as compare to uncatalyzed reaction? Assume other thing being equal.

(a) Double (b) 28 times

(c) 7.38 times (d) 7.38×10^3 times

10. The rate law for one of the mechanism of the pyrolysis of CH_3CHO at 520°C and 0.2 bar is

$$\text{Rate} = -\left(k_2 \left(\frac{k_1}{2k_4} \right)^{1/2} \right) [CH_3CHO]^{1/2}$$

The overall activation energy E_2 in terms of the rate laws is

(a) $E_a(2) + E_a(1) + 2E_a(4)$ (b) $E_a(2) + \frac{1}{2}E_a(1) - E_a(4)$

(c) $E_a(2) + \frac{1}{2}E_a(1) - E_a(4)$ (d) $E_a(2) + \frac{1}{2}E_a(1) + \frac{1}{2}E_a(4)$

11. Difference between activation energies of the reverse the forward steps of a reversible reaction is 9.212RT. If the pre-exponential factor of the forward reaction is double that of the reverse reaction at the same temperature, the equilibrium constant for the reaction at the temperature will be (ln 10=2.303)

(a) 1×10^{-4} (b) 2×10^{-4}

(c) 1×10^{-4} (d) 2×10^{-4}

12. For a reaction, the rate constant k at 27°C was found to be $k = 5.4 \times 10^{11}\ e^{-50}$. The activation energy of the reaction is

(a) 50 J mol^{-1} (b) 415 J mol^{-1}

(c) 15,000 J mol^{-1} (d) 125,000 J mol^{-1}

13. According to Arrhenius equation (k = rate constant and T = temperature)

(a) ln k decreases linearly with 1/T

(b) ln k decreases linearly with T

(c) ln k increases linearly with 1/T

(d) ln k increases linearly with T

14. A first order gaseous reaction is 25% complete in 30 minutes at 227°C and in 10 minutes at 237°C. The activation energy of the reaction is closest to (R = 2 cal K^{-1} mol^{-1})

(a) 27 kcal mol^{-1} (b) 110 kcal mol^{-1}

(c) 55 kcal mol^{-1} (d) 5.5 kcal mol^{-1}

15. The temperature-dependence of a reaction is given by $k = AT^2 \exp(-E_0 / RT)$. The activation energy (E_a) of the reaction is given by

(a) $E_0 + \frac{1}{2}RT$ (b) E_0

(c) $E_0 + 2RT$ (d) $2E_0 + RT$

16. A reaction A + B + C $\rightarrow$ D follows the mechanism

$A + B \rightleftharpoons AB$

$AB + C \rightarrow D$

in which first step remains essentially in equilibrium. If ΔH is the enthalpy change for the first reaction and E_0 is the activation energy for the second reaction, the activation, the activation energy of the overall reaction will be given by

(a) E_0 (b) $E_0 - \Delta H$

(c) $E_0 + \Delta H$ (d) $E_0 + 2\Delta H$

17. The activation energy for the biomolecular reaction A + BC $\rightarrow$ AB + C is E_0 in the gas phase. If the reaction is carried out in a confined volume of λ^3 , the activation energy is expected to

(a) remains unchanged (b) increase with decreasing λ

(c) decrease with decreasing λ (d) oscillate with decreasing λ

18. For a reaction with an activation energy of 49.8 kJ mol^{-1}, the ratio of the rate constants at 600 K and 300K, (k_{600}/k_{300}), is approximately (R = 8.3 J mol^{-1} K^{-1})

(a) ln (10) (b) 10

(c) 10 + c (d) e^{10}

19. If the pre-exponential factor in Arrhenius equation is 1.6×10^{12} s^{-1}, the value of the rate constant at extremely high temperature will be close to

(a) 1.6×10^{12} s^{-1} (b) 4.2×10^{12} s^{-1}

(c) 2.4×10^{9} s^{-1} (d) 1.2×10^{6} s^{-1}

20. Arrhenius equations for two chemical reactions are : $k_1 = A_1 e^{-E_1/RT}, k_2 = A_2 e^{-E_a/RT}, E_1 > E_2$, then at a given temperature T,

(a) $\frac{k_1}{k_2} < \frac{A_1}{A_2}$ (b) $\frac{k_2}{k_1} < \frac{A_2}{A_1}$

(c) $k_1 k_2 > A_1 A_2$ (d) $k_1 + k_2 < A_1 + A_2$

• • • • •

Answers

1. (b) 2. (d) 3. (c) 4. (d) 5. (a) 6. (d) 7. (d) 8. (b) 9. (c) 10. (c) 11. (b) 12. (d) 13. (a) 14. (c) 15. (c)

16. (c) 17. (c) 18. (d) 19. (a) 20. (a)

QUANTA CHEMISTRY

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CHEMICAL KINETICS

DPP-11

1. The collision theory of reaction rates

   1. Assumes that the rate depends on the frequency at which reactants collide.

   2. Assumes that the reactants are perfectly oriented.

   3. Shows how temperature affects the rate.

   4. Assumes that only collision with energy above the activation energy are successful.

   (a) Only 1, 2 and 3 are correct (b) Only 1, 3 and 4 are correct

   (c) Only 2, 3 and d are correct (d) All are correct

2. In collision theory for chemical reaction, which of the following statements is TRUE?

   (a) The molecules are assumed to have 3N–6 vibrational degrees of freedom one of which leads to the reaction.

   (b) The molecules have only translational degrees of freedom and only the relative translational energy of the two colliding partners is important for the reaction.

   (c) One of the rotational degrees of freedom for the molecule leads to the reaction.

   (d) Motion of electrons in the reactants lead to the reaction.

3. Consider the unimolecular reaction A (g) $\rightarrow$ products for which the following remarks were made.

   (A) The reaction is second order at low pressure and becomes first order at high pressure.

   (B) The reaction is first order at low pressure and becomes second order at high pressure.

   (C) The reaction is zero order. Which of the these is correct?

   (a) A and B (b) B and C

   (c) Only C (d) Only A

4. In the collision theory, the preexponential factor is:

   (a) Independent of temperature (b) Proportional to temperature

   (c) Proportional to square of temperature (d) Proportional to square root of temperature

5. If experimentally observed rate constant is less than the value of rate constant obtained using hard-sphere model of collision theory then relation between the impact parameter (b) and sum of the radii of two reactants is

(a) $b = r_1 + r_2$ (b) $b < r_1 + r_2$

(c) $b > r_1 + r_2$ (d) $b \leq r_1 + r_2$

6. For the bimolecular elementary reaction A + A $\rightarrow$ products. The number of collision per unit volume according to collision theory is equal to

(a) $\frac{1}{\sqrt{2}}\pi\sigma^2\bar{u}N_A^2$ (b) $\frac{1}{\sqrt{2}}\pi\sigma^2\bar{u}N_A$

(c) $\frac{3}{\sqrt{2}}\pi\sigma^2\bar{u}N_A$ (d) $\frac{3}{\sqrt{2}}\pi\sigma^2\bar{u}N_A^2$

7. Consider the statements in accordance with the collision theory

(1) Collision theory consider only translational degree of freedom

(2) Value of orientation factor ρ is successfully related to physical properties and structure of the molecules

(3) Reactant molecules are considered to be hard spheres

(4) Redistribution of energy is taken into account

Correct statements is/are

(a) (1), (2) & (3) (b) (1) & (3)

(c) (2) & (4) (d) (1), (3) & (4)

8. The rate constant of a unimolecular reaction was 2.66×10^{-3} s^{-1} and 2.2×10^{-1} s^{-1} at T = 120K and 360K respectively. The rate constant (in s^{-1} units) at 240 K would be

(a) 2.4×10^{-2} (b) 2.4×10^{-1}

(c) 4.8×10^{-2} (d) 1.8×10^{-3}

9. One of the assumptions made in the conventional activated complex theory is:

(a) Equilibrium is maintained between reactants and the activated complex

(b) Equilibrium is maintained between reactants and the products

(c) Equilibrium is maintained between the products and the activated complex

(d) Equilibrium is maintained between the reactants, the activated complex and the products.

10. The Arrhenius parameters for the thermal decomposition of NOCl , $2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$, are $A = 10^{13}$ M^{-1} s^{-1}, E_a = 105 kJ mol^{-1} and RT = 2.5 kJ mol^{-1}. The enthalpy (in kJ mol^{-1}) of the activated complex will be

(a) 110 (b) 105

(c) 102.5 (d) 100

11. Observe the following statements

(I) In the H_2–O_2 reaction, explosion occurs when the rate of chain branching exceeds that of chain termination.

(II) The order of the reaction, nA $\rightarrow$ products, is 2.5 For this reaction, $t_{\frac{1}{2}} \propto [A]_0^{-3/2}$

(III) Unimolecular gas phase reactions are second order at low pressure but becomes first order at high pressure. Which of the following is correct?

(a) I, II and III are correct (b) Only II is correct

(c) Only III is correct (d) I and II are correct

12. In the Lindemann mechanism of unimolecular reactions, the observed order at low concentration is

(a) 0.5 (b) 1

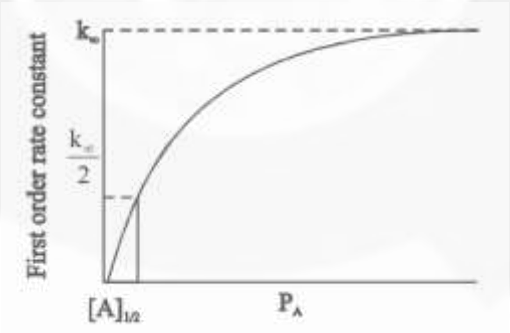
(c) 1.5 (d) 2

13. Species A undergoes a unimolecular reaction as follows :

$A + A \xrightarrow{k_1} A^* + A$

$A^* \xrightarrow{k_1} P$

For this reaction, the first order rate constant at high pressure is k_∞ . The first order rate constant becomes $\frac{k_\infty}{2}$ when pressure of A is $[A]_{1/2}$.



The value of k_1 will be

(a) $\frac{k_\infty}{[A]_{1/2}}$ (b) $k_\infty [A]_{1/2}$

(c) $k_\infty - [A]_{1/2}$ (d) $[A]_{1/2}/ k_\infty$

14. The first order rate constant for a unimolecular gas phase reaction A $\rightarrow$ products that follows Lindemann mechanisms is 2.0 s^{-1} at pA = 1 atm and 4.0 s^{-1} at P_A = 2 atm. The rate constant for the activation step is

(a) 1.0 $atm^{-1}s^{-1}$ (b) 2.0 $atm^{-1}s^{-1}$

(c) 4.0 $atm^{-1}s^{-1}$ (d) 8.0 $atm^{-1}s^{-1}$

15. According to the transition state theory, the plot with slope equal to $\frac{\Delta H}{R}$ is

(a) $\ln k$ vs. T

(b) $\ln\left(\frac{k}{T}\right)$ vs. T

(c) $\ln\left(\frac{k}{T}\right)$ vs. $\frac{1}{T}$

(d) $\ln k$ vs. $\frac{1}{T}$

16. For two reactions,

$X(g)+Y(g)\rightarrow Z(g)$ ..... (1)

$M(g)+N(g)\rightarrow P(g)$ ..... (2)

According to the collision theory, the ratio of squares of pre-exponential factors of reactions 2(A_2) and 1(A_1) at the same temperature,

Species	Mass (g/mol)	Diameter (nm)
X	5	0.3
Y	20	0.5
M	10	0.4
N	10	0.4

(a) 4/5

(b) 5/5

(c) 5/3

(d) 3/5

17. For the reaction, $A+B \rightleftharpoons X^{\#}\rightarrow P$, E_a = 20.0 kJ mol^{-1} at 300K. The enthalpy change for the formation of the activated complex from the reactants in kJ mol^{-1} is

(a) 12

(b) 15

(c) 23

(d) 25

18. According to conventional transition state theory, for elementary biomolecular reactions, the molar entropy of activation $\Delta S^{\#}$ is

(a) Positive

(b) Zero

(c) Negative

(d) Positive for endothermic and negative for exothermic reactions.

19. According to Eyring state theory for a biomolecular reaction, the activated complex has

(a) no vibrational degrees of freedom

(b) vibrational degrees of freedom but they never participate in product formation

(c) one high frequency vibration that leads to product formation

(d) one low frequency vibration that leads to product formation

20. For a gas phase unimolecular reaction at temperature 298K, with a pre-exponential factor of $2.17 \times 10^{13} s^{-1}$, the entropy of activation (JK^{-1} mol^{-1}) is _____

• • • • •

Answers

1. b 2. a 3. d 4. d 5. b 6. a 7. B 8. d 9. a 10. d 11. a 12. d 13. a 14. B 15. d 16. d 17. a 18. d 19. d 20. (2.65 to 3.15)

QUANTA CHEMISTRY

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CHEMICAL KINETICS

DPP-12

1. The absorbance of solution having 20% transmittance is:

   (a) 0.301 (b) 0.699

   (c) 1.301 (d) 1.699

2. A solution of a compound shows a transmittance of 0.800 in a 1.0 cm cell at 525 nm. The transmittance in a 5.0 cm cell at the same wavelength would be

   (a) 0.160 (b) 0.654

   (c) 0.240 (d) 0.327

3. A dye solution of concentration 26 μM shows the optical density of 0.5 in a 1 cm quartz call at 400 nm. The molar extinction coefficient of the dye is given by

   (a) 1923.077 M^{-1} mm^{-1} (b) 52 M^{-1} cm^{-1}

   (c) 13000 M^{-1} mm^{-1} (d) Cannot be calculated

4. A solution containing 5 ppm of $KMnO_4$ (F.W. = 159) has a transmittance of 0.360 measured in a 1 cm cell at 500 nm. The molar absorptivity of $KMnO_4$ in L mol^{-1} cm^{-1} is :

   (a) 1.1×10^4 (b) 1.4×10^4

   (c) 1.9×10^4 (d) 2.7×10^4

5. A solution containing 47 ppm of a compound X (FW 225) has a transmittance of 29.7% in a 1.5 cm cell at 400 nm. The molar absorptivity in L mol^{-1} cm^{-1} is:

   (a) 1.89×10^3 (b) 1.42×10^3

   (c) 1.68×10^3 (d) 1.79×10^3

6. "Phosphorescence" is represented as

   (a) $T_1 \rightarrow S_0 + h\nu$ (b) $T_1 \rightarrow S_0 + \Delta$

   (c) $S_1 \rightarrow S_0 + h\nu$ (d) $S_1 \rightarrow T_0 + \Delta$

7. The following mechanism was proposed for the photolysis of HI into H_2 and I_2.

   $HI + h\nu \rightarrow H + I$; $H + HI \rightarrow H_2 + I$; $2I \rightarrow I_2$

(a) 0.5 (b) 1

(c) 2 (d) 4

8. In the mechanism of reaction, $H_2 + Br_2 \longrightarrow 2HBr$ the first step is

(a) dissociation of H_2 into H radicals (b) dissociation of Br_2 into Br radicals

(c) reaction of H radical with Br_2 (d) reaction of Br radical with H_2

9. The mechanism of photochemical reaction between H_2 and B_2 is similar to that established for the thermal reaction. The mechanism is

(i) $Br_2 \xrightarrow{hv} 2Br$ (ii) $Br + H_2 \xrightarrow{k_2} HBr + H$

(iii) $H + Br_2 \xrightarrow{k_3} HBr + Br$ (iv) $H + HBr \xrightarrow{k_4} H_2 + Br$

(iv) $Br + Br \xrightarrow{k_5} Br_2$

The quantum efficiency of HBr formation is

(a) $\frac{1}{I_{abs}^{1/2}} \frac{k_2 (1/k_5)^{1/2} [H_2]}{1 - (k_4 [HBr]/k_3 [Br_2])}$ (b) $\frac{1}{I_{abs}^{1/2}} \frac{k_2 (1/k_5)^{1/2} [H_2]}{1 + (k_4 [HBr]/k_3 [Br_2])}$

(c) $\frac{1}{I_{abs}^{1/2}} \frac{k_2 (1/k_5)^{1/2} [H_2]}{(k_4 [HBr]/k_3 [Br_2])}$ (d) $\frac{1}{I_{abs}^{1/2}} \frac{k_2 (1/k_5)^{1/2} [H_2]}{(k_4 [HBr]/[Br_2])}$

10. The proposed mechanism of photochemical reaction between CO and Cl_2

(i) $Cl_2 \xrightarrow{hv} 2Cl$ (ii) $Cl + CO \xrightarrow{k_2} COCl$

(iii) $COCl \xrightarrow{k_3} CO + Cl$ (iv) $COCl + Cl_2 \xrightarrow{k_4} COCl_2 + Cl$

(v) $COCl + Cl \xrightarrow{k_5} CO + Cl_2$

The quantum efficiency of Cl_2 deformation is

(a) $k_4\left(\frac{k_2[CO]^{1/2}}{k_3k_5I_{abs}}\right)^{1/2}[Cl_2]$ (b) $\left(\frac{k_2[CO]^{1/2}}{k_3k_5I_{abs}}\right)^{1/2}[Cl_2]$

(c) $k_4\left(\frac{[CO]^{1/2}}{k_3k_5I_{abs}}\right)^{1/2}[Cl_2]$ (d) $k_4\left(\frac{k_2[CO]^{1/2}}{k_3I_{abs}}\right)^{1/2}[Cl_2]$

11. The proposed mechanism is

$CH_3CHO \xrightarrow{hv} CH_3 + CHO$

$CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO$

$CH_3CO \xrightarrow{k_3} CO + CH_3$

$CH_3 + CH_3 \xrightarrow{k_4} C_2H_6$

The quantum efficiency of CO formation is

(a) $k_2\left(\frac{1}{2k_4I_{abs}}\right)[CH_3CHO]$ (b) $k_2\left(\frac{1}{k_4I_{abs}}\right)^2[CH_3CHO]$

(c) $k_2\left(\frac{1}{2k_4I_{abs}}\right)^{1/2}[CH_3CHO]$ (d) $k_2\left(\frac{1}{k_4I_{abs}}\right)^{1/2}[CH_3CHO]$

12. The proposed mechanism is

$H_2O_2 \xrightarrow{hv} 2OH$

$OH + CO \xrightarrow{k_2} COOH$

$COOH + H_2O_2 \xrightarrow{k_3} CO_2 + H_2O + OH$

$H_2O_2 + OH \xrightarrow{hv} H_2O + HO_2$

$2HO_2 \xrightarrow{k_5} O_2 + H_2O_2$

The quantum efficiency for H_2O_2 deformation is

(a) $2\left(1 + \frac{k_2[CO]}{k_4[H_2O_2]}\right)$ (b) $\left(1 + \frac{k_2[CO]}{k_4[H_2O_2]}\right)$

(c) $2\left(1-\frac{k_2[CO]}{k_4[H_2O_2]}\right)$ (d) $\left(1-\frac{k_2[CO]}{k_4[H_2O_2]}\right)$

13. For the gaseous reaction

$Cl_2 + CH_3Cl_3 \xrightarrow{hv} CCl_4 + HCl$

the proposed mechanism is

$Cl_2 \xrightarrow{hv} 2Cl$

$Cl + CHCl_4 \xrightarrow{k_2} CCl_3 + HCl$

$CCl_3 + Cl_2 \xrightarrow{k_3} CCl_4 + Cl$

$2CCl_3 + Cl_2 \xrightarrow{k_4} 2CCl_4$

The quantum efficiency for Cl_2 deformation is

(a) $2-k_3\left(\frac{[Cl_2]}{I_{abs}K_4}\right)^{1/2}$ (b) $2-k_3\left(\frac{[Cl_2]}{I_{abs}K_4}\right)^{1/2}$

(c) $3+k_3\left(\frac{[Cl_2]}{I_{abs}K_4}\right)^{1/2}$ (d) $2+k_3\left(\frac{[Cl_2]}{I_{abs}K_4}\right)^{1/2}$

14. Photochemical decomposition of HI takes place with the following mechanism.

$HI + hv(I_\alpha) \longrightarrow H + I$

$H + HI \xrightarrow{hv} H_2 + I$

$I + I + M \xrightarrow{k_2} I_2 + M$

Considering hydrogen (H) and iodine (I) atoms as intermediates, the rate of removal of HI is

(a) $\frac{I_a}{2}$ (b) I_a

(c) $2I_a$ (d) I_a^2

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Answers

1. (b) 2. (d) 3. (a) 4. (b) 5. (c) 6. (a) 7. (c) 8. (b) 9. (b) 10. (a) 11. (c) 12. (a) 13. (d) 14. (c)

QUANTA CHEMISTRY

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CHEMICAL KINETICS

DPP-13

1. For a second order reaction A+ B $\rightarrow$ products, where the initial concentration of the reactants are the same (x mol/lit) and k is the rate constant, the half life of the reaction is :

   (a) 1/kx (b) 0.693 K

   (c) 0.5/k (d) 0.5 kx

2. For a first order reaction, the half-life is 50s. Identify the correct statement form the following.

   (a) The reaction is complete in 100s

   (b) The reaction begins after 50s

   (c) The same quantity of A is consumed for every 50s of the reaction.

   (d) Quantity of A remaining after 100s is half of what remains after 50s.

3. If the concentration vs time plot is found to be linear with a negative slope, the order of the reaction is:

   (a) 0 (b) 1

   (C) 2 (d) Cannot be determined

4. Consider the plots for the types of reaction, nA $\rightarrow$ B + C

   These plots respectively correspond to the reaction orders :

   (a) 0, 2, 1 (b) 0, 1, 2

   (c) 1, 1, 2 (d) 1, 0, 2

5. If the concept of half-life is generalized to quarter-life of a first order chemical reaction, it will be equal to

   (a) $\frac{\ln 2}{k}$ (b) $\frac{\ln 4}{k}$

   (c) $\frac{4}{k}$ (d) $\frac{1}{4k}$

6. For a first order reaction A $\rightarrow$ products, the plot of $\ln\left(\frac{|A|_n}{|A|_0}\right)$ vs time, where $[A]_0$ and $[A]_t$ refer to concentration at time t = 0 and t respectively, is

   (a) a straight line with a positive slope passing through origin

   (b) a straight line with a negative slope passing through origin

   (c) an exponential curve asymptotic to the time axis

   (d) an exponential curve symptotic to the time axis

7. For a reaction, 2A + B $\rightarrow$ 3Z, if the rate of consumption of A is 2×10^{-1} mol dm^{-3} s^{-1} the rate of formation of Z (in mol dm^{-3} s^{-1}) will be

(a) 3×10^{-4} (b) 2×10^{-4}

(c) $\frac{4}{3} \times 10^{-4}$ (d) 4×10^{-4}

8. Half-life $t_{1/2}$ for a third order reaction 3C $\rightarrow$ products, where C_0 is the initial concentration of C, will be

(a) $\frac{3}{2kC_0^2}$ (b) $\frac{1}{kC_0}$

(c) $\frac{3}{2kC_0}$ (d) $\frac{2}{2kC_0^2}$

9. In kinetic study of a chemical reaction, slopes are drawn at different times in the plot of concentration of reactants versus time. The magnitude of slope with increase of time

(a) remains unchanged

(b) increases

(c) decreases

(d) increases and decreases periodically

10. If the unit of the rate constant of a reaction is $L^3mol^{-3}s^{-1}$, the order of the reaction is

(a) 1 (b) 2

(c) 3 (d) 4

11. For a given first order reaction, the reactant reduces to 1/4th its initial value in 10 minutes. The rate constant of the reaction is :

(a) 0.1386 min^{-1}

(b) 0.0693min^{-1}

(c) 0.1386 mol L^{-1} min^{-1}

(d) 0.0693 mol L^{-1} min^{-1}

12. In the following reaction A$\rightarrow$B+C, rate constant is 0.001 Ms^{-1}. If we start with 1 M of A then conc. Of A and B after 10 minutes are respectively

(a) 0.5 M, 0.5 M (b) 0.6 M, 0.4 M

(c) 0.4 M, 0.6 M (d) None of these

13. For the reaction $2X_3 = 3X_2$, the rate of formation of X_2 is :

(a) $3\left(-d[X_3]/dt\right)$ (b) $\frac{1}{2}\left(-d[X_3]/dt\right)$

(c) $\frac{1}{3}\left(-d[X_3]/dt\right)$ (d) $\frac{3}{2}\left(-d[X_3]/dt\right)$

14. For the reaction : $Br_2(g) + BF_2(g) \rightarrow 2BrF_3(g)$, the equilibrium constant at 2000 K and 1.0 bar is 5.25. When the pressure is increased by 8-fold, the equilibrium constant.

(a) Increase by a factor of 1.86

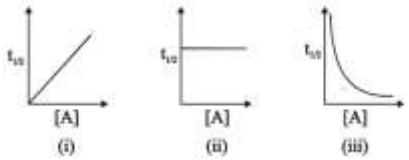
(b) Decrease by a factor of 1.86

(c) Remains same

(d) Increases by a factor of 8

15. Consider the plots, gives below, for the types of reaction:

$nA \rightarrow B + C$



These plots respectively correspond to the reaction orders :

(a) 0, 1, 2 (b) 1, 2, 0

(c) 1, 0, 2 (d) None of these

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Answers

1. (a) 2. (d) 3. (a) 4. (d) 5. (b) 6. (b) 7. (a) 8. (a) 9. (c) 10. (d) 11. (a) 12. (c) 13. (a) 14. (c) 15. (c)

QUANTA CHEMISTRY

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Assignment Sheet – Chemical Kinetics

1. The rate constant of a unimolecular reaction was 2.66×10^{-1} and 2.2×10^{-1} at T = 120K and 360 K respectively. The rate constant (in 1 s^{-1} units) at 240 K would be
   (a) 2.4×10^{-2} (b) 2.4×10^{-1}
   (c) 4.8×10^{-2} (d) 1.8×10^{-3}
2. The overall rate of the following complex reaction,

$$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A_2 \quad \text{(fast equilibrium)}$$

$$A + B \underset{}{\overset{k_2}{\rightleftharpoons}} C \quad \text{(fast equilibrium)}$$

$$A_2 + C \underset{}{\overset{k_3}{\rightleftharpoons}} P + 2A \quad \text{(slow)}$$

   by steady state approximation would be
   (a) $K_1K_2k_3[A]_3[B]$ (b) $K_2K_1k_3[A][B]_3$
   (c) $K_1K_2k_3[A][B]_2$ (d) $K_1K_2k_3[A][B]$
3. The concentration of a reactant undergoing decomposition was 0.1, 0.08 and 0.067 mol L^{-1} after 1.0, 2.0 and 3.0 hr respectively. The order of the reaction is
   (a) 0 (b) 1
   (c) 2 (d) 3
4. At any temperature for the following reaction (D and T are deuterium and tritium respectively) correct statement is:
   (A) HCI + F → HF + Cl, (B) DCI + F → DF + CI (C) TCI + F → TF + Cl
   (a) (A) is fastest (b) (B) is fastest
   (c) (C) is fastest (d) All the above reactions have the same rate constant
5. An example of a relaxation method of measuring rates is:
   (a) Spectroscopic monitoring of product concentration.
   (b) Stopped flow technique
   (c) Temperature jump experiments.
   (d) Measurement of spectral line widths.

6. The half-life of a zero order reaction (A → P) is given by (k = rate constant):
   (a) $t_{1/2} = \dfrac{[A]_0}{2k}$ (b) $t_{1/2} = \dfrac{2.303}{k}$
   (c) $t_{1/2} = \dfrac{[A_0]}{k}$ (d) $t_{1/2} = \dfrac{1}{k[A_0]}$
7. The decomposition of gaseous acetaldehyde at T(K) follows second order kinetics. The half-life of this reaction is 400 s when the initial pressure is 250 Torr. What will be the rate constant (in

$Torr^{-1}s^{-1}$) and half-life (in s) respectively, if the initial pressure of the acetaldehyde is 200 Torr at the same temperature?

(a) 10^5 and 500 (b) 10^{-5} and 400

(c) 10^{-4} and 400 (d) 10^{-5} and 500

8. For an enzyme catalyzed reaction, a Lineweaver-Burk plot gave the following data:
slope = 40 s , intercept = 4 (m mol $dm^{-3}s^{-1})^{-1}$.
If the initial concentration of enzyme is 2.5×10^{-9} mol dm^{-3}, what is the catalytic efficiency (in dm^{-3} $mol^{-1}s^{-1}$) of the reaction?

(a) 10^5 (b) 10^6

(c) 10^7 (d) 10^4

9. Observe the following aqueous solutions of same compound. All the measurements are made at same wavelength and same temperature.
Solution A: The transmittance of 0.1 mol dm^{-3} using 1 cm cell is 0.5.
Solution B: The optical density 0.5 mol dm^{-3} is measured using 1 mm cell.
Solution C: The transmittance of this solution is 0.1.
The optical density of these solutions follow the order. (log 20 = 1.3010; log 30 = 1.4771, log 50 = 1.6990

(a) A > B > C (b) B > C > A

(c) B >A > C (d) C > A > B

10. For a reaction, the rate constant k at 27°C was found to be $k = 5.4 \times 10^{11}\ e^{-50}$. The activation energy of the reaction is:

(a) 1 50 J mol^{-1} (b) 1 415 J mol^{-1}

(c) 1 15,000 J mol^{-1} (d) 1 125,000 J mol^{-1}

11. The rate law for one of the mechanism of the pyrolysis of CH_3CHO at 520°C and 0.2 bar is

$$\text{Rate} = -\left|k_2\left(\frac{k_1}{2k_1}\right)^{1/2}\right|\left[CH_3CHO\right]^{3/2}$$

The overall activation energy E, in terms of the rate law is:

(a) Ea(2) + Ea(1) + 2Ea(4) (b) $\text{Ea}(2)+\frac{1}{2}\text{Ea}(1)-\text{Ea}(4)$

(c) $\text{Ea}(2)+\frac{1}{2}\text{Ea}(1)-\frac{1}{2}\text{Ea}(4)$ (d) $\text{Ea}(2)-\frac{1}{2}\text{Ea}(1)-\frac{1}{2}\text{Ea}(4)$

12. In the Michaelis-Menten mechanism for enzyme kinetics, the expression obtained is:

$$\frac{v}{[E]_0[S]} = 1.4\times10^{12} - \frac{10^4 v}{[E]_0}$$

The values of k_3 (K_{ems}, mol $L^{-1}s^{-1}$) and K (Michaelis constant, mol L^{-1}), respectively are

(a) 1.4×10^{12}, 10^4 (b) 1.4×10^8, 10^4

(c) 1.4×10^8, 10^{-4} (d) $1.4 \times 10_{12}$, 10_{-4}

13. One of the assumptions made in the conventional activated complex theory is:
(a) Equilibrium is maintained between reactants and the activated complex
(b) Equilibrium is maintained between the reactants and the products.
(c) Equilibrium is maintained between the products and the activated complex
(d) Equilibrium is maintained between the reactants, the activated complex and the products.

14. The quantitative determination of N_2H_4 with KIO_3 proceeds in a mixture of H_2O/CCI_4 as Follows

$N_2H_4 + KIO_3 + 2HCI \rightarrow N_2 + KCI + ICI + 3H_2O$

The end point for the titrimetric reaction is:

(a) Consumption of

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(b) ICI formation
(c) Disappearance of the Yellow colour due to Cl_2 in CCI_4 layer.
(d) Displacement of the Red colour due to I_2 in CCl_4 layer

15. The carbon-14 activity of an old wood sample is found to be 14.2 disintegrations min^{-1} g^{-1}.Calculate age of old wood sample, if for a fresh wood sample carbon-14 activity is 15.3 disintegrations $min^{-1}g^{-1}$($t_{1/2}$ carbon-14 is 5730 years), is:
(a) 5,000 years (b) 4,000 years
(c) 877 years (d) 617 years

16. "Phosphorescence" is represented as
(a) $T_1 \rightarrow S_0 + hv$ (b) $T_1 \rightarrow S_0 + \Delta$
(c) $S_1 \rightarrow S_0 + hv$ (d) $S_1 \rightarrow T_1 + \Delta$

17. Using cuvettes of 0.5 cm path length, a 10^{-4} M solution of a chromophore shows 50% transmittance at certain wave length. The molar extinction coefficient of the chromophore at this wave length is (log 2 = 0.301)
(a) 1500 M^{-1} cm^{-1} (b) (b) 3010 M^{-1} cm^{-1}
(c) (c) 5000 M^{-1} cm^{-1} (d) 6020 M^{-1} cm^{-1}

18. If the concept of half-life is generalized to quarter-life of a first order chemical reaction, it will be equal to
(a) $\frac{\ln 2}{k}$ (b) $\frac{\ln 4}{k}$
(c) $\frac{4}{k}$ (d) $\frac{1}{4k}$

19. The activation energy for the bimolecular reaction A + BC → AB + C is E_0 in the gas phase. If the reaction is carried out in a confined volume of λ_3, the activation energy is expected to:
(a) Remain unchanged (b) Increase with decreasing λ
(c) Decrease with decreasing λ (d) Oscillate with decreasing λ

20. The decomposition of NH_3 on Mo surface follows Langmuir-Hinshelwood mechanism. The decomposition was carried out at low pressures. The initial pressure of NH_3 was 10^{-2} torr. The pressure of NH_3 was reduced to 10^{-4} torr in 10 minutes. The rate constant of decomposition of NH_3 is:
(a) 9.9×10^{-4} torr min^{-1} (b) 0.4606 min^{-1}
(c) 9.9×10^{-3} torr min^{-1} (d) 0.693 min^{-1}

21. In atom recombination reactions
(a) $E_a = 0$, $\Delta S^{\#}$ = +ve, $\Delta H^{\#}$ = +ve (b) $E_a = 0$, $\Delta S^{\#}$ = -ve, $\Delta H^{\#}$ = = -ve
(c) E_a = +ve, $\Delta S^{\#}$ = -ve, $\Delta H^{\#}$ = -ve (d) E_a = +ve, $\Delta S^{\#}$ = +ve, $\Delta H^{\#}$ = +ve

22. A radioisotope ^{41}Ar initially decays at the rate of 34, 500 disintegrations/minute, but decay rate falls to 21, 500 disintegrations/minute after 75 minutes. The $t_{1/2}$ for ^{41}Ar is:
(a) 90 minutes (b) 110 minutes
(c) 180 minutes (d) 220 minutes

23. Observe the following statements
(I) In the H_2–O_2 reaction, explosion occurs when the rate of chain branching exceeds that of chain termination.
(II) The order of the reaction, nA → products, is 2.5. For this reaction, $t_{1/2} \propto [A]_0^{-3/2}$
(III) Unimolecular gas phase reactions are second order at low pressure but become first order at high pressure.
Which of the following is correct?
(a) I, II and III are correct (b) Only II is correct
(c) Only III is correct (d) I and II are correct

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24. The concentrations of a species A undergoing the reaction A → P is 1.0, 0.5, 0.33, 0.25 mol dm^{-3} at t = 0, 1, 2 and 3 seconds, respectively. The order of the reaction is:
(a) two (b) one
(c) zero (d) three

25. In the Lindemann mechanism of unimolecular reactions, the observed order at low concentration is:
(a) 0.5 (b) 1
(c) 1.5 (d) 2

26. A bacterial colony grows most commonly by cell division. The change in the population due to cell division in an actively growing colony is dN = AN dt. The population of bacterial colony at time 't' is [N_0 = N(t = 0)]
(a) N t (b) N_0 exp [-]
(c) N_0 exp [21] (d) N_0 $(21)^2$

27. The rate equation for the reaction 2AB+B2 → $2AB_2$ is given by rate = k[AB] [B_2]
A possible mechanism consistent with this rate law is
(a) $2AB + B_2 \xrightarrow{\text{slow}} 2AB_2$
(b) AB+AB ⇋ A2B2 (fast) ; $A_2B_2 + B_2 \xrightarrow{\text{slow}} 2AB_2$
(c) $AB + B_2 \xrightarrow{\text{slow}} AB_3$; $AB_3 + AB \xrightarrow{\text{fast}} 2AB_2$
(d) AB+B2 ⇋ AB3 (fast) ; $AB_3 + AB \xrightarrow{\text{slow}} 2AB_2$

28. A 0.1 M solution of compound A shows 50% transmittance when a cell of 1cm width is used at λ nm. Another 0.1 M solution of compound B gives the optical density value of 0.1761 using 1 cm cell at λ_1 nm .What will be the transmittance of a solution that is simultaneously 0.1 M in A and 0.1 M in B using the same cell and at the same wave length? [log 20 = 1.301; log 30 = 1.4771; log 50 =1.699]
(a) 33.3% (b) 50%
(c) 66.7% (d) 70%

29. A chemical reaction involving nonlinear molecule + nonlinear molecule ⇋ nonlinear activated complex .The number of vibrational degrees of freedom in the activated complex, containing N atoms, is
(a) 3N-5 (b) 3N-6
(c) 3N-7 (d) 3N-8

30. According to Arrhenius equation (k = rate constant and T = temperature)
(a) ln k decreases linearly with 1/T (b) ln k decreases linearly with T
(c) ln k increases linearly with 1/T (d) ln k increases linearly with T

31. A first order gaseous reaction is 25% complete in 30 minutes at 227₀C and in 10 minutes at 237°C. The activation energy of the reaction is closest to (R = 2 cal K^{-1} mol^{-1})
(a) 27 kcal mol^{-1} (b) 110 kcal mol^{-1}
(c) 55 kcal mol^{-1} (d) 5.5 kcal mol^{-1}

32. In the reaction between NO and H_2 the following data are obtained
Experiment I: PH_2 constant

P_{NO} (mm of Hg)	359	300	152
$\frac{-dP_{NO}}{dt}$	1.59	1.03	0.25

Experiment II : P_{NO} = constant

P_{H_2} (mm of Hg)	289	205	147
$\frac{-dP_{H_2}}{dt}$	1.60	1.10	0.79

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The orders with respect to H_2 and NO are
(a) 1 with respect to NO and 2 with respect to H_2
(b) 2 with respect to NO and 1 with respect to H_2
(c) 1 with respect to NO and 3 with respect to H_2
(d) 2 with respect to NO and 2 with respect to H_2

33. Examine the following first order consecutive reactions. The rate constant (in s^{-1} units) for each step is given above the arrow mark

(A) $P \xrightarrow{10^5} Q \xrightarrow{10^3} R$ (B) $P \xrightarrow{10^5} Q \xrightarrow{10^3} R$

(C) $P \xrightarrow{10^7} Q \xrightarrow{10^7} R$ (D) $P \xrightarrow{10^2} Q \xrightarrow{10^5} R$

Steady-state approximation can be applied to
(a) A only (b) C only
(c) B and C only (d) A and D only

34. In the Lineweaver-Burk plot of $(\text{initial rate})^{-1}$ vs. $(\text{initial substrate concentration})^{-1}$ for an enzyme catalysed reaction following Michaelis-Menten mechanism, they-intercept is 5000 M^{-1} s. If the initial enzyme concentration is 1×10^{-9} M, the turnover number
(a) 2.5×10^3 (b) 1.0×10^4
(c) 2.5×10^4 (d) 2.0×10^5

35. The fluorescence lifetime of a molecule in a solution is 5×10^{-9} s. The sum of all the nor adiative rate constants (Σk_{nr}) for the decay of excited state is $1.2 \times 10^8\ s^{-1}$. The fluorescence quantum yield of the molecule is
(a) 0.1 (b) 0.2
(c) 0.4 (d) 0.6

36. For a first order reaction A→ products, the plot of $\ln\left(\frac{[A]_t}{[A]_0}\right)$ ***vs*** time , where $[A]_0$ and $[A]_t$ to concentration at time = 0 and t respectively, is
(a) a straight line with a positive slope passing through origin
(b) a straight line with a negative slope passing through origin.
(c) an exponential curve asymptotic to the time axis
(d) a curve asymptotic to the $\ln\left(\frac{[A]_t}{[A]_0}\right)$

37. For an enzyme-substrate reaction, a plot between 1/v and $1/[S_0]$ yields a slope of 40 s. If the enzyme concentration is 2.5 μM, then the catalytic efficiency of the enzyme is
(a) 40 $Lmol^{-1}\ s^{-1}$ (b) $10^{-4}\ Lmol^{-1}\ s^{-1}$
(c) $10^7\ Lmol^{-1}\ s^{-1}$ (d) $10^4\ Lmol^{-1}\ s^{-1}$

38. For a gaseous reaction, $2NO(g) + Cl_2(g) \rightarrow$ Non-linear T.S. $\rightarrow 2NOCl$
the pre-exponential factor in the rate constant is proportional to
(a) $T^{1/2}$ (b) $T^{-1/2}$
(c) $T^{-5/2}$ (d) $T^{-7/2}$

39. The rate constant for a reaction $A^{3+} + B^{n+1} \rightarrow P$ is measured in two different aqueous solutions of ionic strengths 0.01 M and 0.04 M. If log K0.04/K0.01 = 0.3, the charge n on B is closest to
(a) 1 (b) 2
(c) 3 (d) 6

40. A reaction A + B + C D follows the mechanism
$A + B \leftrightharpoons AB$
$AB + C \rightarrow D$

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in which first step remains essentially in equilibrium. If ΔH is the enthalpy change for the first reaction and E_0 is the activation energy for the second reaction, the activation energy of the overall reaction will be given by

(a) E_0 (b) $E_0 - \Delta H$

(c) $E_0 + \Delta H$ (d) $E_0 + 2\Delta H$

41. Which of the following will result in deviation from Beer's law ?

1. Change in refractive index or medium.
2. Dissociation of analyte on dilution.
3. Polychromatic light.
4. Path length of cuvette.

(a) 1, 2 and 3 (b) 2, 3 and 4

(c) 1,3 and 4 (d) 1, 2 and 4

42. The temperature-dependence of a reaction is given by $k = AT_2 \exp(-E_0/RT)$
The activation energy E_a of the reaction is given by:

(a) $E_0 + ½ RT$ (b) E_0

(c) $E_0 + 2RT$ (d) $2E_0 + RT$

43. For a reaction, $2A + B \rightarrow 3Z$, if the rate of consumption of A is 2×10^{-4} mol $dm^{-3}s^{-1}$ the rate of formation of Z (in mol dm^{-3} s^{-1}) will be

(a) 3×10^{-4} (b) 2×10^{-4}

(c) $4/3 \times 10^{-4}$ (d) 4×10^{-4}

44 The equilibrium constants for the reactions $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$ and $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ are K_1 and K_2, respectively. The equilibrium constant for the reaction $CH_4(g) + H_2O(g) \rightleftharpoons CO_2(g) + 3H_2(g)$ is

(a) $K_1 . K_2$ (b) $K_1 - K_2$

(c) K_1/K_2 (d) $K_2 - K_1$

45. For a given ionic strength, (I) rate of reaction is given by $\log\frac{k}{k_0} = -4 \times 0.51\, I^{1/2}$. Which of the following reactions follows the above equation?

(a) $S_2O_8^{2-} + I^-$ (b) $Co(NH_3)_5 Br^{2+} + OH^-$

(c) $CH_3COOC_2H_5 + OH^-$ (d) $H^+ + Br^- + H_2O_2$

46. The intensity of a light beam decreases by 50% when it passes through a sample of 1.0 cm path length. The percentage of transmission of the light passing through the same sample, but of 3.0 cm path length, would be

(a) 50.0 (b) 25.0

(c) 16.67 (d) 12.5

47 .Considering the following parameters with reference to the fluorescence of a solution :

1. Molar absorptivity of fluorescent molecule.
2. Intensity of light source used for excitation.
3. Dissolved oxygen

The correct answer for the enhancement of fluorescence with the increase in these parameters is/are

(a) 1 and 2 (b) 2 and 3

(c) 1 and 3 (d) 3 only

48. According to transition state theory, the temperature-dependence of pre-exponential factor (A) for a reaction between a linear and a non-linear molecule, that forms products through a nonlinear transition state, is given by

(a) T (b) T^2

(c) T^{-2} (d) $T^{-1.5}$

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49. In a photochemical reaction, radicals formed according to the equation

$C_4H_{10} + hv \leftrightharpoons 2C_2H_5$

$C_2H_5 + C_2H_5 \xrightarrow{k_2} C_2H_6 + C_2H_4$

If I is the intensity of light absorbed, the rate of the overall reaction is proportional to-

(a) I (b) $I_{1/2}$

(c) $I[C_4H_{10}]$ (d) $I_{1/2}[C_4H_{10}]_{1/2}$

50. For the following reaction,

$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2B \; ; \; B \xrightarrow{k_2} C$

$\frac{d[B]}{dt}$ is given by

(a) $k_1[A] - k_{-1}[B]_2 - 2k_2[B]$ (b) $2k_1[A] - k_{-1}[B]_2 - k_2[B]$

(c) $1/2\ k_1[A] - 1/2\ k_{-1}[B]_2 - k_2[B]$ (d) $2k_1[A] - 2k_{-1}[B]_{1/2} - k_2[B]$

51. According to the transition state theory, one of the vibrations in the activated complex is a loose vibration. The partition function for this loose vibration is equal to (k_B is the Boltzmann's constant and h is the Planck's constant)

(a) k_BT/h (b)hv/k_BT

(c) k_BT (d) k_BT/hv

52. v_{max} and K_m for an enzyme catalyzed reaction are 2.0×10^{-3} Ms^{-1} and 1.0×10^{-6} M, respectively. The rate of the reaction when the substrate concentration is 1.0×10^{-6} M is

(a) $3.0 \times 10^{-3}\ s^{-1}$ (b) $1.0 \times 10^{-3}\ s^{-1}$

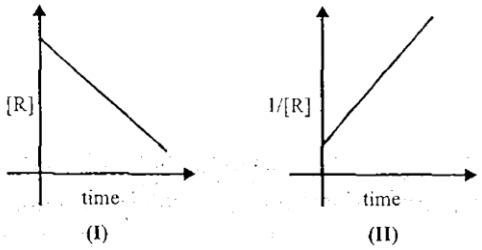
(c) $2.0 \times 10^{-3}\ s^{-1}$ (d) $0.5\ s^{-1}$

53. The first order rate constant for a unimolecular gas phase reaction A → products that follows indemann mechanism is $2.0\ s^{-1}$ at $p_A = 1$ atm and $4.0\ s^{-1}$ at $p_A = 2$ atm. The rate constant for the activation step is

(a) $1.0\ atm^{-1}s^{-1}$ (b) $2.0\ atm^{-1}s^{-1}$

(c) $4.0\ atm^{-1}s^{-1}$ (d) $8.0\ atm^{-1}s^{-1}$

54. The concentration of a reactant R varies with time for two different reactions as shown in the following plots :



The orders of these two reactions I and II, respectively, are –

(a) zero and one (b) one and zero

(c) zero and two (d) two and zero

55. If the rates of a reaction are R_1 and R_2 at concentrations C_1 and C_2 of a reactant respectively, the order of reaction, 'n' (assuming that the concentrations of all other reactants and T remain constant) with respect to that reactant is given by

(a) $n = \frac{\log R_1 - \log R_2}{\log C_1 - \log C_2}$ (b) $n = \frac{\log C_1 - \log C_2}{\log R_1 - \log R_2}$

(c) $n = \frac{\log C_1 - \log R_1}{\log C_2 - \log R_2}$ (d) $n = \frac{\log C_2 - \log R_2}{\log C_1 - \log R_1}$

Q56. Experimentally determined rate law for the chemical reaction,

$2NO_2F \rightarrow 2NO_2 + F_2$ is $R = k[NO_2F]$

The rate determining step consistent with the rate law is

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(a) $2NO_2F \rightarrow 2NO_2 + F_2$ (b) $NO_2F + F \rightarrow NO_2 + F_2$

(c) $NO_2F \rightarrow NO_2 + F$ (d) $NO_2 + F \rightarrow NO_2F$

Q57. For the chemical reaction in aqueous solution,

$CH_2ClCOO^- + OH^- \rightarrow CH_2OHCOO^- + Cl$ the correct statement is

(a) increase of pressure increases the rate constant

(b) increase of dielectric constant increases the rate constant

(c) increase of ionic strength decreases the rate constant

(d) the entropy of activation is positive

Q58.If experimentally observed rate constant is greater than the maximum value of rate constant obtained using hard-sphere model of collision theory, then relation between the impact parameter (b) and sum of the radii of two reactants is

(a) $b = r_1 + r_2$ (b) $b < r_1 + r_2$

(c) $b > r_1 + r_2$ (d) $b \leq r_1 + r_2$

Q59. Half-life $t_{½}$ for a third order reaction $3C \rightarrow$ products, where C_0 is the initial concentration of C, will be

(a) $\frac{3}{2kC_0^2}$ (b) $\frac{3}{kC_0}$

(c) $\frac{3}{2kC_0}$ (d) $\frac{2}{3kC_0^2}$

Q60.For a reaction with an activation energy of 49.8 kJ mol^{-1}, the ratio of the rate constants at 600 K and 300 K, (k_{600}/k_{300}), is approximately ($R = 8.3$ J mol^{-1} K^{-1})

(a) ln 10 (b) 10

(c) 10 + e (d) e^{10}

Q61. According to the transition state theory, the plot with slope equal to $\frac{\Delta H^{\neq}}{R}$ is

(a) ln k vs. T (b) $\ln\frac{k}{T}$ vs T

(c) $\ln\frac{k}{T}$ vs $\frac{1}{T}$ (d) ln k vs. $\frac{1}{T}$

Q62. A reaction goes through the following elementary steps

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2C \quad \text{(fast)}$$

$$A + C \xrightarrow{k_2} D \quad \text{(slow)}$$

Assuming that steady state approximation can be applied to C, on doubling the concentration of A, the rate of production of D will increase by (assume $K_2[A] << K^{-1}[C]$)

(a) 2 times (b) 4 times

(c) 8 times (d) $2\sqrt{2}$ times

Q63. For two reactions

$X(g) + Y(g) \rightarrow Z(g)$ (1)

$M(g) + N(g) \rightarrow P(g)$ (2)

according to the collision theory, the ratio of squares of pre-exponential factors of reactions 2 (A_2) and 1 (A_1) at the same temperature $\left(\frac{A_2}{A_1}\right)^2$

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Species	Mass (g/mol)	Diameter (mm)
X	5	0.3
Y	20	0.5
M	10	0.4
N	10	0.4

(a) 4/5 (b) 5/5
(c) 5/3 (d) 3/5

Q64.The rate of an acid-catalyzed reaction in aqueous solution follows the rate equation
$r = k[X^+][Y^{2-}][H^+]$
If k_{16} and k_4 are rate constants for the reaction at ionic strength of 16 mol L^{-1} and 4 mol L^{-1}, respectively $\ln\frac{k_4}{k_{16}}$, in terms of Debye-Huckel constant (B = 0.51) , is
(a) 4B (b) 8B
(c) 10B (d) 12B

Q65.If the pre-exponential factor in Arrhenius equation is 1.6×10^{12} s^{-1}, the value of the rate constant at extremely high temperature will be close to
(a) 1.6×10^{12} s^{-1} (b) 4.2×10^{12} s^{-1}
(c) 2.4×10^{9} s^{-1} (d) 1.2×10^{6} s^{-1}

Q66.In kinetic study of a chemical reaction, slopes are drawn at different times in the plot of concentration of reactants versus time. The magnitude of slopes with increase of time
(a) remains unchanged (b) increases
(c) decreases (d) increases and decreases periodically

Q67. Photochemical decomposition of HI takes place with the following mechanism
$HI + hv\ (I_a) \longrightarrow H + I$
$H + HI \xrightarrow{k_1} H_2 + I$
$I + I + M \xrightarrow{k_2} I_2 + M$
Considering hydrogen (H) and iodine (I) atoms as intermediates, the rate of removal of HI is
(a) $I_a/2$ (b) I_a
(c) $2I_a$ (d) $I_a 2$

Q68. In a enzyme catalyzed reaction:
$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P$
$k_2 = 3.42\times10^4 s^{-1}$. If $[E]_0 = 1.0 \times 10^{-2}$ mol dm^{-3}, the magnitude of maximum velocity and turn over number using Michaelis-Menten kinetics are
(a) $3.42\times10^2\ mol\,dm^{-3}s^{-1}; 3.42\times10^4 s^{-1}$ (b) $3.42\times10^6\ mol\,dm^{-3}s^{-1}; 3.42\times10^4 s^{-1}$
(c) $3.42\times10^4\ mol\,dm^{-3}s^{-1}; 3.42\times10^6 s^{-1}$ (d) $3.42\times10^4\ mol\,dm^{-3}s^{-1}; 3.42\times10^2 s^{-1}$

Q69.Arrhenius equations for two chemical reactions are: $k_1 = A_1 e^{-E_1/RT}, k_2 = A_2 e^{-E_2/RT}$. If $E_1 > E_2$ then at a given temperature T
(a) $\frac{k_1}{k_2} < \frac{A_1}{A_2}$ (b) $\frac{k_2}{k_1} < \frac{A_2}{A_1}$
(c) $k_1 k_2 > A_1 A_2$ (d) $k_1 + k_2 > A_1 + A_2$

Q70. For a sequence of consecutive reactions, $A \xrightarrow{k_1} I \xrightarrow{k_2} P$, the concentration of I would be, by steady state approximation.
(a) $k_1[A]$ (b) $(k_1 + k_2)[A]$
(c) $k_1 k_2 [A]$ (d) $\frac{k_1}{k_2}[A]$

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Q71. The slope and intercept obtained from (1/Rate) against (1/substrate concentration) of an enzyme catalyzed reaction are 300 and 2×10^5, respectively. The Michaelis-Menten constants of the enzyme in this reaction is

(a) 5×10^6 M (b) 5×10^{-6} M

(c) 1.5×10^3 M (d) 1.5×10^{-3} M

Q72. Reaction between A and B is carried out for different initial concentrations and the corresponding half-life times are measured. The data listed in the table:

Entry	$[A_0]$ (μM)	$[B_0]$ (μM)	$t_{1/2}$ (sec)
1	500	10	60
2	500	20	60
3	10	500	60
4	20	500	30

(a) $k[A][B]^2$ (b) $k[A]^2$

(c) $k[A]^2[B]$ (d) $k[A][B]^2$

Q73. Elementary steps of a reaction are as follows

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2C$$

$$2C \xrightarrow{k_2} D$$

If steady state approximation is applicable to C, the rate of product formation in the reaction is

(a) proportional to [A][B] (b) proportional to $[A]^2[B]^2$

(c) proportional to $[A]^{1/2}[B]^{1/2}$ (d) independent of [A][B]

Q74. For an enzyme-substrate reaction,

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

the slope and intercept of plot between 1/r and 1/[S] are 10^{-2} s and 10^2 $M^{-1}s$, respectively, If $E_0 = 10^{-6}M$ and $\frac{k_{-1}}{k_2} = 1000$, the value of k_1 will be close to (in units of $M^{-1}s^{-1}$) [r is the rate of reaction and E_0 is initial concentration of enzyme

(a) 1×10^{11} (b) 1×10^4

(c) 1×10^8 (d) 1×10^6

Q75. Difference between-activation energies of the reverse and forward steps of a reversible reaction is 9.212 RT. If the pre-exponential factor of the forward reaction is double that of the reverse reaction at the same temperature, the equilibrium constant for the reaction at that temperature will be (ln 10 = 2.303)

(a) 1×10^4 (b) 2×10^4

(c) 1×10^{-4} (d) 2×10^{-4}

76. For a second-order reaction, the straight line among the following plots is

(a) [X] versus time (b) 1/[X] versus time

(c) log[X] versus 1/time (d) log[X] versus time

77. If the half-life of a reaction is inversely proportional to the square of the concentration of the reactant, the order of the reaction is

(a) 0 (b) 1

(c) 2 (d) 3

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78. The gas phase decomposition of A at 1000K follows two decomposition paths .

	Elementary Process	Rate Constant
(i)	$A \rightarrow B + C$	$3\ s^{-1}$
(ii)	$A \rightarrow P + Q$	$5\ s^{-1}$

The maximum theoretical percentage yield of P at 1000K is

(a) 62.5 (b) 60

(c) 166 (d) 37.5

79. Photochemistry of a molecule, M, is described as by the mechanism

	Elementary Process	Rate Constant
(i)	$M + h\nu \rightarrow M^{\bullet}$	I_{abs}
(ii)	$M^{\bullet} + Q \rightarrow M + Q$	$k_Q[Q][M^{\bullet}]$
(iii)	$M^{\bullet} \rightarrow M + h\nu_F$	$0.2[M^{\bullet}]$

The intercept at [Q] = 0 is 4 for the inverse of fluorescence intensity $\left(\frac{I}{I_F}\right)$ vs [Q] plot.

The value of I_{abs} is

(a) 4 (b) 0.25

(c) 20 (d) 0.8

80. If the rate constant for a base catalyzed ester hydrolysis reaction is 0.20 L $mol^{-1}s^{-1}$, half-life (in s) of the ester (Given $[ester]_0 = [base]_0 = 0.05$ mol L^{-1}) would be closest to

(a) 40 (b) 100

(c) 140 (d) 200

81. The rate constant of a second order reaction $2A \rightarrow Z$ is k_2. If the initial concentration of the reactant is a_0 and the concentration of the product at time t is x, then a linear function of t with the slope k_2a_0 is

(a) $\ln\left(\frac{x}{a_0 - x}\right)$ (b) $\frac{x}{a_0(a_0 - x)}$

(c) $\frac{x}{2(a_0 - x)}$ (d) $\ln\left(\frac{x}{a_0(a_0 - x)}\right)$

82. The oxidation of NO to NO_2 occurs via the mechanism given below

$$2NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$$

$$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$$

$\frac{d[NO_2]}{dt}$ in the presence of large excess of O_2 can be written as

(a) $2k_1(NO)_2$ (b) $2k_1k_2(NO)_2(O_2)$

(c) $\frac{k_1}{k_2}(NO)^2$ (d) $2k_2(NO)^2$

83. Substance 'A' is exposed to 600 nm, 100 W light source for 6626 s, with 50% of the incident light being absorbed. 'A' decomposes according to the reaction $A \rightarrow 2B$. As a result of irradiation, 0.2 mol B is produced. The quantum yield of the reaction is closest to

Options:

(a) 6×10^6 (b) 6×10^{-4}

(c) 6×10^{-2} (d) 6

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84. The concentration (C) of a compound undergoing decomposition as a function of time (t) is given below:

t/min	0	1	2	4	6
C/M	1.00	0.80	0.67	0.50	0.40

The order of the reaction is

Options:

(a) 0 (b) 1

(c) 2 (d) 3

85. For a reaction, raising the temperature from 200 K to 300 K results in the increase of rate constant by a factor of 2. The activation energy for this reaction in kJ mol^{-1} is closest to (ln 2 = 0.69)

Options:

(a) 7.0 (b) 3.5

(c) 14.0 (d) 0.83

86. The rate constant for the reaction $A_2B_4O \rightarrow AB_4 + AO$, is described as,

$$\log k = 14.1 - \frac{10000\,K}{T}$$

the activation energy (in kJ mol^{-1}) is closest to

(a) 191.4 (b) 83.14

(c) 382.8 (d) 166.28

87. The rate of decomposition of a gas is 10 mM s^{-1} when 10% is reacted and it is 5 mM s^{-1} when 40% is reacted. The order of the reaction is:

(a) 2 (b) 1.71

(c) 0 (d) 2.15

88. For a person weighing 70 kg the minimal volume (in mL) of a fatal dose of a compound with LD_{50} = 80 mg. kg^{-1}, and density = 1.45 g. mL^{-1} is

(a) 5.6 (b) 3.9

(c) 0.8 (d) 0.4

89. For the reaction,

$$[\text{cis-M(en)}_2(\text{OH})_2]^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\text{trans-M(en)}_2(\text{OH})_2]^+$$

the equilibrium constant is 0.16 and k_1 is $3.3 \times 10^{-4} s^{-1}$. The experiment is started with pure cis form. The time taken for half the equilibrium amount of trans isomer to be formed is about

(a) 290 s (b) 580 s

(c) 190 s (d) 480 s

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ANSWER KEY

CHEMICAL KINETICS

1	2	3	4	5	6	7	8	9	10
A	A	C	A	C	A	D	C	D	D
11	12	13	14	15	16	17	18	19	20
C	C	A	D	D	A	D	B	C	B
21	22	23	24	25	26	27	28	29	30
B	B	A	A	D	A	C	A	C	A
31	32	33	34	35	36	37	38	39	40
C	B	D	D	C	B	D	D	C	C
41	42	43	44	45	46	47	48	49	50
A	C	A	C	B	D	D	D	D	D
51	52	53	54	55	56	57	58	59	60
D	B	B	C	A	C	B	C	A	D
61	62	63	64	65	66	67	68	69	70
C	D	A	D	A	C	C	A	A	D
71	72	73	74	75	76	77	78	79	80
D	C	A	A	B	B	A	A	B	B
81	82	83	84	85	86	87	88	89	
C	A	C	C	B	A	B	B	A	

QUANTA CHEMISTRY